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(54) RAW MATERIAL ALLOY FOR RARE EARTH MAGNET AND ITS PRODUCTION

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a raw material powder for magnet excellent in a magnetic property by forming a low heat conduction layer on a roll surface so as to suppress the generation of a fine chill crystal structure in a solidified raw material for magnet when producing a raw material for a R-T-B magnet by a rapid solidifying method by using a cooling roll.

SOLUTION: When producing a raw material for a R-T-B magnet, a molten metal of the alloy is rapidly cooled/solidified in an inert gas atmosphere of Ar, etc., or a vacuum with a twin roll method, etc., to be pulverized. In this case, a surface layer of 0.1-10 mm thickness, which is made of a material having a low coefficient of heat conduction of Ni, Cr, alumina, etc., is formed on a surface of a rapid cooling roll, which is made of a material having a good coefficient of heat conduction of Cu, etc. Due to presence of the surface layer, the generation of a fine chill crystal is suppressed to a structure of the R-T-B alloy to be cooled/solidified. By setting its generation rate to $\leq 5\%$, a magnetic property of the R-T-B magnet, which is obtained by crushing the alloy and forming/sintering, is improved.

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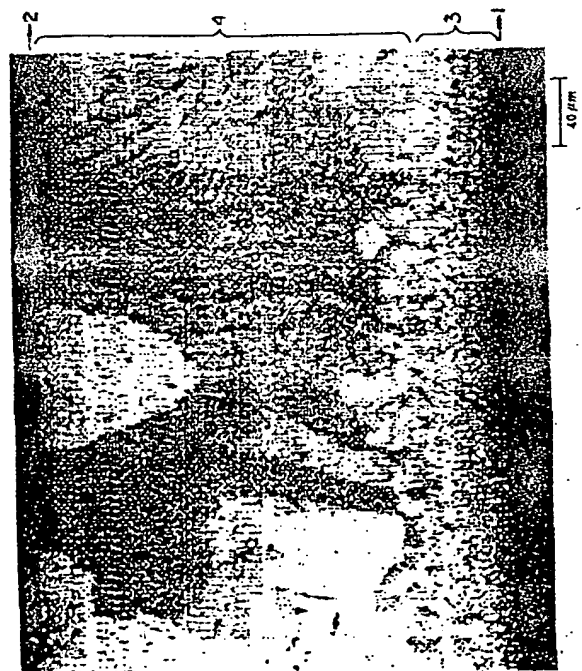
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(54) 【発明の名称】 希土類系磁石用原料合金とその製造方法

(57) 【要約】

【課題】 冷却用ロールを用いた急冷凝固法により製造されるR-T-B系磁石用原料合金において、その粉碎時に粒径1 μ m以下の微細粉の発生の低減が可能な当該原料合金並びにその製造方法の提供。

【解決手段】 冷却用ロール表面に基材よりも熱伝導率の小さな材料による特定厚みの表面層を設けて緩冷却化を図ることにより、微細なチル晶組織3の生成を抑制でき、断面組織における面積比で5%以下で、且つ残部が均一な柱状晶組織4を有することを特徴とし、その結果、粉碎工程での微粉末の生成を防止して良好な粒度分布の成形用粉末を得ることを可能にした。



【特許請求の範囲】

【請求項1】 冷却用ロールを用いた急冷凝固法により製造されるR-T-B系磁石用原料合金であり、該原料合金のロール面に接触した薄帯表面近傍に生成する微細なチル晶組織の断面組織全体に占める面積比率（チル晶組織の平均生成比率）が5%以下である希土類系磁石用原料合金。

【請求項2】 R-T-B系合金溶湯を冷却用ロールにて急冷凝固させて合金薄帯を得る希土類系磁石用原料合金の製造方法において、冷却用ロールの溶湯冷却面にロール基材よりも熱伝導率の小さい材料からなる表面層を少なくとも0.1mmを超える厚みで形成し、異材質表面層による緩冷却化を施して急冷凝固する希土類系磁石用原料合金の製造方法。

【請求項3】 請求項2において、表面層厚みが0.1mmを超え、10mm以下である希土類系磁石用原料合金の製造方法。

【発明の詳細な説明】

【0001】

【産業上の利用分野】この発明は、冷却用ロールを用いた急冷凝固法により製造される種々組成のR-T-B系磁石用原料合金の製造に係り、ロール表面に基材よりも熱伝導率の小さな材料による特定厚みの表面層を設けて緩冷却化し、得られる合金薄片のロール面側表面近傍に生成する微細なチル晶組織の量を少なく、すなわち、微細なチル晶組織の合金薄片の厚み断面に占める割合を5%以下となすことにより、合金薄片の微粉砕時に発生する微細粉末を減少させ、所定の粒度分布からなり磁気特性の向上が期待できる磁石用合金粉末の製造を可能にした、希土類系磁石用原料合金とその製造方法に関する。

【0002】

【従来の技術】近年、高性能な希土類（R）系統結磁石であるNd-Fe-B系統結磁石は様々な分野で使用されている。例えば、ハードディスク装置など電子機器の内部に組み込まれるモーターをはじめ核磁気共鳴断層撮影装置（MRI）のような医療機器の磁界発生源などに、その需要は拡大するとともに、更なる高性能化の要求も増大している。かかる背景の中で、磁石特性の向上を目的とした原料合金の製造技術とそれによる原料合金に関しいくつかの提案がなされている。

【0003】当初は、溶湯を鑄型に鑄込んだインゴットを粉砕、焼結して磁石を製造していたが、インゴット外周部と中心部では組織が著しく異なること、結晶粒が粗大であること及び粗大なFeが析出する等の問題があった。鑄造インゴットを粉砕して得た原料合金を用いて磁石化した場合、磁石粒子間及び磁石粒子内の希土類元素に不都合な偏在があり、磁石特性を劣化させるとともに、製造面でも焼結性、粉砕性、及び原料歩留まりを悪化させていた。

【0004】かかる問題に対する解決策として、急冷ロ

ールを用いた急冷凝固法に関するいくつかの提案がなされている。特開昭60-89546号では急冷することにより5μm以下の正方晶組織を得ることにより優れた保磁力を持つ磁石を製作することができるとしている。また、特開昭63-317643号では、急冷ロールを用いて得られる原料合金の柱状晶結晶粒径、鑄造板厚を規定して、得られる磁石の高性能化を図った製造方法が提案されている。

【0005】特開平5-222488号、特開平5-295490号及び特開平7-66022号には、急冷ロールによる製造条件、すなわち冷却速度、過冷度、冷却方向等を規定して適正な柱状組織を得ようとした製造方法が提案されている。

【0006】さらに、特開平4-55042号、特開平5-135919では、ロール外周部にCrメッキ層を10～100μmで被覆してロールの耐久性を改善するとともに、適正な結晶粒径をより得やすくしようとした製造方法が提案されている。

【0007】

【発明が解決しようとする課題】一方、R-T-B系統結磁石の磁気特性の向上を考えると、鑄造インゴットを粉砕して得た場合も急冷ロールを用いて得られる薄帯合金を粉砕した原料合金を用いる場合も、粉砕時に発生する粒径1μm以下の微細粉は、酸化されやすくまた結晶粒径より小さいことにより磁石特性を悪化させ、原料歩留まりの低下をもたらすことが指摘されている。

【0008】前述の冷却用ロールを用いた急冷凝固法により製造されるR-T-B系磁石用原料合金は、いずれも磁石の高性能化を図ることができるが、粉砕時に粒径1μm以下の微細粉の発生を防止することはできないものであった。さらなる磁石特性の向上には微細粉の除去が必要となるが、容易なことではなく、粉砕時に微細粉の発生が少ない原料合金が求められている。

【0009】この発明は、冷却用ロールを用いた急冷凝固法により製造されるR-T-B系磁石用原料合金において、その粉砕時に粒径1μm以下の微細粉の発生の低減が可能な当該原料合金並びにその製造方法の提供を目的としている。

【0010】

【課題を解決するための手段】発明者らは、急冷凝固法による希土類系薄帯合金の粉砕時における粒径1μm以下の微細粉の発生を解決するために、R-T-B系合金磁石用原料合金の急冷凝固組織を調査した結果、粉砕工程時に微細粉発生の要因として、ロール急冷による急冷時、主として鑄造片のロールと接触する側に図1及び図2に示すような等軸微細なチル晶組織が生成されており、この微細チル晶が粉砕工程において微細粉末を生成することを知見した。

【0011】そこで、発明者らは、粉砕時の微細粉発生の原因である、ロールと接触する側に生成される微細チ

ル晶組織の生成防止を図るために種々検討を重ねた結果、次の1)～9)の点に着目し、この発明を完成させた。

【0012】1) 従来、一般的に用いられている冷却ロールの材質は純銅またはこれに近い銅合金であり、熱伝導率が高い。

2) 鋳片の断面凝固組織のうち、ロール表面近傍領域においては凝固時の冷却速度が大きいために、過冷度も大きく、凝固の核生成速度が大きい。

3) 急冷凝固鋳片の断面組織のうち、核生成速度の大きいロール面側近傍領域には、微細なチル晶組織が生成しやすい。

4) 微細なチル晶組織の生成を防止するためにはロールの冷却面における材質を銅又は銅合金に比較して熱伝導率の低い材質に変更することが効果的である。

5) 一方、冷却用ロールそのものの材質を全て一様に熱伝導率の低いものに変更することは水冷によるロールの冷却効率の観点から望ましくない。

6) そこで、銅ロールの表面部分の材質のみを熱伝導率の低い材質に変更する、すなわち、表面改質による緩冷却化が効果的である。

7) 6)の方法によって製造される希土類系磁石原料合金の凝固組織においては、チル晶の生成率が低く、ロール面側から自由表面側に向かって均一な柱状晶組織を生成している。

8) 6)の方法によって微粉末の生成が抑制され、粉碎工程における歩留まりが改善され、また均一な粒度分布が得られる。

9) 6)の方法によって製造される希土類系磁石用原料合金を粉碎、成型、焼結して得られる焼結磁石は良好な磁気特性を有する。

【0013】すなわち、この発明は、冷却用ロールを用いた急冷凝固法により製造されるR-T-B系磁石用原料合金であり、該原料合金のロール面に接触した薄帯表面近傍に生成する微細なチル晶組織の断面組織全体に占める面積比率(チル晶組織の平均生成比率)が5%以下である希土類系磁石用原料合金である。

【0014】また、この発明は、R-T-B系合金溶湯を冷却用ロールにて急冷凝固させて合金薄帯を得る希土類系磁石用原料合金の製造方法において、冷却用ロールの溶湯冷却面にロール基材よりも熱伝導率の小さい材料からなる表面層を少なくとも0.1mmを超える厚みで形成し、異材質表面層による緩冷却化を施して急冷凝固する希土類系磁石用原料合金の製造方法である。

【0015】
[発明の実施の形態] この発明により製造されるR-T-B系磁石用原料合金の組成は、希土類元素(R)、遷移金属元素(T)およびBを主成分とし、適宜選定される種々の添加元素、その他に溶製上不可避免的な不純物元素により構成されるものである。これは、この発明によ

る永久磁石を優れた磁気特性を示す $R_2T_{14}B_1$ の原子比からなる正方晶の主磁性相と粒界に偏析して焼結工程において液相焼結を促進する役割を果たすRに富んだRリッチ相の2相でもって構成させるためである。

【0016】Rは、具体的には、Ndを主成分とし、PrやDy等の希土類元素を含有してもよく、その組成範囲(Rの合計)は10原子%～30原子%が望ましい。10原子%未満では十分な保磁力(IHc)が得られず、また30原子%超えると十分な残留磁束密度(B_r)が得られないからである。さらに望ましいRの範囲は、12～15原子%である。

【0017】Tは、具体的にはFeを主成分とし、Coを含有してもよく、その組成範囲は、42原子%～88原子%である。42原子%未満では十分な残留磁束密度が得られず、また88原子%超えると十分な保磁力が得られないからである。さらに望ましいTの範囲は、77～84原子%である。Coによる置換は永久磁石の耐熱性および耐食性向上に効果的である。

【0018】Bの組成範囲は、2原子%～28原子%である。2原子%未満では十分な保磁力が得られず、また28原子%超えると十分な残留磁束密度B_rが得られないからである。さらに望ましいTの範囲は、4～8原子%である。

【0019】さらに、前記R、B、Fe合金あるいはCoを含有するR-Fe-B合金に、9.5原子%以下のAl、4.5原子%以下のTi、9.5原子%以下のV、8.5原子%以下のCr、8.0原子%以下のMn、5原子%以下のBi、12.5原子%以下のNb、10.5原子%以下のTa、9.5原子%以下のMo、9.5原子%以下のW、2.5原子%以下のSb、7原子%以下のGe、3.5原子%以下のSn、5.5原子%以下のZr、5.5原子%以下のHfのうち少なくとも1種添加含有させることにより、永久磁石合金の高保磁力が可能になる。この発明のR-Fe-B系永久磁石において、結晶層は主層が正方晶であることが不可欠であり、特に、微細で均一な合金粉末を得て、すぐれた磁気特性を有する焼結永久磁石を作製するのに効果的である。

【0020】この発明は、上述の組成になるように配合した合金溶湯を、常法に従ってArガスのような不活性雰囲気中あるいは真空中において、急冷ロールを用いて急冷凝固させてR-T-B系磁石用原料合金を製造するに際して、特に冷却用ロールの溶湯接触面を表面改質することにより緩冷却化を図ることを特徴としている。その理由は、後の粉碎工程において微粉末を生成する要因となる微細なチル晶組織の生成を抑制するためである。

【0021】すなわち、急冷ロール本体に銅や銅合金のような熱伝導率の高い材料を用いることが多いが、溶湯の冷却効果が過大となり、鋳片のロール面側近傍に等軸微細なチル晶組織が生成しやすいが、ロールの表面に

ール材質よりも熱伝導率の低い材料でもって表面改質を施すことによって微細なチル晶の生成を抑制することができる。

【0022】冷却用ロールの表面層の材料としては、Ni、Mo、Cr、WC-Co、アルミナ、TiN、SiC、AlN、Si₃N₄、ジルコニア、Ni-50Cr、Co-23Cr-12Al-0.5Y、Co-32Ni-21Cr-8Al-0.5T、Ni-22Cr-10Al-1Y、Co-28Cr-4W-3Fe-1C、Co-28Mo-17Cr-3Si、WC-27NiCr、Al₂O₃-3TiO₂、Al₂O₃-2.5ZrO₂-2TiO₂、Al₂O₃-2.2Si、ZrO₂-8Y₂O₃、ZrO₂-2.5MgO、WC-14CoCr、Cr₃C₂-2.5NiCr、ZrO₂-3.3SiO₂、Cr₃C₂、TiC、ZrC、ZrB₂が効果的であり、もちろん、これらの材質を積層して複合的に用いてもよい。これらの材質が効果的な理由は、いずれの材質も銅や銅ベリリウムなどの銅を主成分とする合金に比較して熱伝導率が低いため、緩冷却化の効果が得られやすいからである。

【0023】Niおよび/またはCrによる表面改質にはメッキ法が望ましい。また、Mo、WC-Co、アルミナ、TiN、SiC、AlN、Si₃N₄、ジルコニア、Ni-50Cr、Co-23Cr-12Al-0.5Y、Co-32Ni-21Cr-8Al-0.5T、Ni-22Cr-10Al-1Y、Co-28Cr-4W-3Fe-1C、Co-28Mo-17Cr-3Si、WC-27NiCr、Al₂O₃-3TiO₂、Al₂O₃-2.5ZrO₂-2TiO₂、Al₂O₃-2.2Si、ZrO₂-8Y₂O₃、ZrO₂-2.5MgO、WC-14CoCr、Cr₃C₂-2.5NiCr、ZrO₂-3.3SiO₂、Cr₃C₂、TiC、ZrC、ZrB₂による表面改質には溶射が望ましい。その理由は、ロール本体との材質との密着性に優れるために熱伝達が良好であるためである。

【0024】また、これらの表面層は複合的に用いてもよい。すなわち、例えば、ロール面にNi、MoまたはCrを単独であるいは複合的にメッキした後に、さらにその表面に、WC-Co、アルミナ、TiN、SiC、AlN、Si₃N₄、ジルコニア、Ni-50Cr、Co-23Cr-12Al-0.5Y、Co-32Ni-21Cr-8Al-0.5Y、Ni-22Cr-10Al-1Y、Co-28Cr-4W-3Fe-1C、Co-28Mo-17Cr-3Si、WC-27NiCr、Al₂O₃-3TiO₂、Al₂O₃-2.5ZrO₂-2TiO₂、Al₂O₃-2.2Si、ZrO₂-8Y₂O₃、ZrO₂-2.5MgO、WC-14CoCr、Cr₃C₂-2.5NiCr、ZrO₂-3.3SiO₂、Cr₃C₂、TiC、ZrC、ZrB₂を単独であるいは複合的に溶射してもよい。また、金属の複合溶射も効果的である。たとえば、

よい。さらに、金属とセラミックスの複合溶射を施してもよい。たとえば、SiCとNiをダブルトーチを用いて複合溶射してもよく、この場合には溶射後の緻密化処理として熱間静水圧プレス(Hot Isostatic Pressing; HIP)を施すことが好ましい。

【0025】冷却用ロールの表面層の厚みとしては、0.1mm以上、10mm以下の範囲が望ましい。0.1mm以下では合金鍍片の緩冷却化を十分に実現することができず、チル晶が生成してしまうためである。10mmを超えると、凝固組織の粗大化が著しいため、永久磁石に製造した場合に保磁力が低下する問題を生じ、さらに緩冷却化が過ぎるために初晶のγ-Feが晶出し、凝固後の相変態によりα-Fe相が原料合金中に残留して、粉砕特性ひいては磁石特性の低下を招来し好ましくない。この観点から、さらに望ましい表面層の厚み範囲は、Ni、Mo、W-Cu、Fe-Ni-Cu、Ni-50Cr、Co-23Cr-12Al-0.5Y、Co-32Ni-21Cr-8Al-0.5Y、Ni-22Cr-10Al-1Y、Co-28Cr-4W-3Fe-1C、Co-28Mo-17Cr-3Siの場合は0.5mm、アルミナ、TiN、SiC、AlN、Si₃N₄、ジルコニア、Al₂O₃-3TiO₂、Al₂O₃-2.5ZrO₂-2TiO₂、Al₂O₃-2.2Si、ZrO₂-8Y₂O₃、ZrO₂-2.5MgO、WC-14CoCr、Cr₃C₂-2.5NiCr、ZrO₂-3.3SiO₂、Cr₃C₂、TiC、ZrC、ZrB₂の場合は0.1~2mm、WC-Co、WC-27NiCrの場合は0.5~4mmである。

【0026】この発明の希土類磁石用原料合金は、上述の表面層を施した冷却用ロールを用いて製造されるが、その形態は単ロール法によっても双ロール法によってもよい。特に、双ロールを用いる場合には、溶湯の凝固鍍片の両側から進行するためにより均一な柱状晶組織をより厚く形成させることができる。その結果、原料合金の製造効率が向上し、また粉砕特性、磁石特性が向上するという利点がある。

【0027】双ロール法の場合、溶湯の供給方法については、上注ぎ法あるいはタンディッシュを用いる横注ぎ法のいずれであってもよい。ロールのサイズについては、特に限定しないが、製造効率と内部の水冷による冷却効率の観点からは、径が200mm~700mmで、幅が200mm~1000mmであることが望ましい。

【0028】上述のこの発明の冷却用ロールを用いたストリップキャスティング法により製造されるR-T-B系磁石用原料合金は、チル晶の生成率が低く均一な柱状晶組織を有する。具体的には、この発明のR-T-B系磁石用原料合金は、図1及び図2に示すごとく、ロール面側表面1近傍に生成するチル晶組織3の平均生成比率が、断面組織における面積比で5%以下で、且つ、磁石が

均一な柱状晶組織4を有することを特徴とする。さらに望ましくは平均生成比率が2%以下である。

【0029】ここで、この発明ではチル晶組織の平均生成比率について以下のように定義し、判定する。まず、組織観察用試料として、R-T-B系磁石用原料合金の縦断面組織を観察面に検出させ、偏光顕微鏡を用いて500倍で観察する。組織の検出には、原料合金を樹脂等に埋め込み研磨し、縦断面を仕上げバフ研磨により鏡面状に仕上げたものをそのまま用い、特に腐食液等による検出を要しない。観察には走査型電子顕微鏡の反射電子像を用いても良い。偏光像または反射電子像を用いるのはチル晶組織を鮮明に検出させるためである。

【0030】観察する視野は、ロール面側近傍の断面組織を無作為に選択し、図1及び図2のごとき連続する400mm(500倍で)の縦断面組織写真を撮影する。同時に、例えば50倍程度の低倍率で組織写真を撮影しておき、先に観察した領域に対応する原料合金の総断面積を求めておく。次に、500倍で撮影した組織写真の中で、チル晶組織3を呈する領域の面積を求め、先に求めた総断面積との比をもってチル晶組織の生成比率とする。このような方法で、無作為に抽出した合計10個所の断面組織連続写真についてチル晶の生成比率を求め、チル晶組織の平均生成比率とする。

【0031】また、通常柱状晶の1次デンドライトアーム間隔を柱状晶の粒径(又は短軸方向の粒径)としているが、均一な柱状晶組織とは、柱状晶組織の平均1次デンドライトアーム間隔が3~10 μ mとなることである。ここで1次デンドライトアーム間隔は次のように定義し、判定する。まず、組織観察用試料として、R-T-B系磁石用原料合金の縦断面組織を観察面に検出させ、通常の光学顕微鏡を用いて200倍で観察する。組織の検出には、原料合金を樹脂等に埋め込み研磨し、縦断面を仕上げバフ研磨により鏡面状に仕上げたものをそのまま用い、特に腐食液等による検出を要しない。

【0032】観察する視野は、ロール面側近傍の断面組織を無作為に10視野選択し、200倍で縦断面組織写真を撮影する。これらの断面組織写真においてロール面側から20mm(写真上実寸)の位置に直線を引き、その直線を横切る1次アームの数をカウントする。その直線の長さに相当する試料実寸をカウントした数で除し、1次デンドライトアーム間隔とする。

【0033】上述の合金組織を有するR-T-B系磁石用原料合金を得るためには、鋳片の厚みが0.1~10mmであることが望ましい。0.1mm未満では冷却効果が過大となり、チル晶の生成比率が5%を超え、また、10mm以上では冷却効果が十分に発揮されず、凝固組織の粗大化や α -Feの生成を招く問題がある。その観点から、さらに望ましい鋳片の厚みは0.2~5mmである。

磁石用原料合金は以下に述べる粉末冶金工程、すなわち、粉砕、磁場中成形、焼結、熱処理を施すことにより、磁石特性の良好な永久磁石に製造される。

【0035】粉砕には、水素化・脱水素による予備粉砕(水素粉砕)を施すことが好ましい。水素化処理は、R-T-B系磁石用原料合金をチャンバ内等で真空状態においた後、水素ガスを導入し、少なくとも5分以上保持した後にもう一度真空に引き、必要に応じてArガス等不活性ガスで置換し、室温まで冷却することによって処理する。水素化処理の後、脱水素処理を施すことにより、予備粉砕を施す。脱水素処理は100℃~600℃で真空中に30分以上保持した後、室温まで冷却することにより処理する。

【0036】上述の予備粉砕後、ジェットミルによる粉砕を施す。粉砕には乾式あるいは湿式のアトライドあるいはボールミルを用いても良い。粉砕後の平均粉末粒度は2~8 μ mが望ましい。平均粒度が2 μ m未満の微粉末粒子は粉砕中に酸化されやすく、磁石特性を低下させるために使用できず、結果的に歩留まりの低下を招くという問題がある。平均粒度が8 μ m超の粗粉末粒子は焼結磁石の結晶粒組織を粗大にするため、保磁力の低下を招くという問題がある。この観点から、より望ましい平均粒度は2~4 μ mである。

【0037】この発明のR-T-B系磁石用原料合金に上述の一連の粉砕処理を施すことにより、従来材に比べて微粉末の少ない良好な粒度分布特性を有する粉末が得られる。磁場中成形においては、非磁性材料の型、例えばゴム製やオーステナイト系鋼製あるいはマルテンサイト系鋼製の型に上述の方法で得られるR-T-B系磁石用原料合金の粉末を充填し、パルス磁界を印加することによって粉末粒子を配向させた後にプレスにより成形する。またパルス磁界のかわりに静磁界あるいはパルス磁界と静磁界とを組み合わせても良い。

【0038】焼結は、真空中あるいはAr不活性ガス雰囲気中において、1030℃~1150℃で2~4時間処理する。その後必要に応じて450℃~650℃で30~90分の時効熱処理を施すことにより、この発明の永久磁石が製造される。また、この発明により製造された磁石用原料合金はHDDRプロセスへの適用も可能であり、ボンド磁石にも使用可能である。

【0039】

【実施例】

実施例1

表1に示す組成の合金を一旦0.01Torrまで減圧し、Arガスをゲージ圧0.2気圧まで注入した雰囲気中で高周波誘導加熱により溶解した。この溶湯を用いて図3に示す双ロール急冷装置により急冷凝固鋳片を作製した。図3は急冷凝固装置を模式的に示したもので、溶湯をタンデイスシュ5上方より注湯し、タンデイスシュ5内に一旦溜め、注湯するに付て溶湯は本管に注

し。タンデイッシュ堰6より溢れ出てロール8に至る。ロール8は予め図中の矢印の方向に回転しており、ロール8により急冷凝固して急冷凝固鑄片9が作製される。

【0040】ロールの直径は600mmで、その基材は銅ベリリウム合金を用い、その表面層の材質は表2及び表5に示すものとした。またロール間のギャップは1～2mmになるように調整した。なお、この実施例は双ロールを使用した場合で説明するが、単ロールを使用した場合でも同様の効果が得られたことを確認した。

【0041】得られた鑄片を3kg/cm²のH₂ガス雰囲気中に2時間保持して水素化処理し、その後真空中500℃で5時間保持して脱水素処理を施し、室温迄冷却することで予備粉砕とした。磁場成形については、得られた粉末をゴム製の型に充填し、30kOeのパルス磁界を瞬間的に印加することにより粉末を配向させた後に静水圧プレスをした。この成形体を1090℃で3時間で保持して焼結した後、600℃で1時間の時効熱処理を施し、永久磁石を得た。

【0042】この発明の方法により得られた鑄片のチル晶生成率は表3及び表6に示すように、5%以下であり、柱状晶の1次アーム間隔は3.2～7μmとなり、

粉砕後の微細粉生成率は低く、磁石の最大エネルギー積は比較例と較べて大きく良好であった。

【0043】比較例1

急冷ロールの外周面を改質せずに、基材である銅ベリリウム合金のままのものを用いて、実施例と同様な試験を行った。その結果を比較例として表4に示す。デンライト1次アームの間隔は実施例と同様であったが、チル晶の生成率は5%を超えており、微粉生成率も高く、磁石特性も最大エネルギー積は実施例と比較して小さく劣るものであった。

【0044】比較例2

厚さ50μmのCrメッキにより外周面を改質した急冷ロールを用い、実施例と同様の試験を行った。その結果を表4に示す。Crメッキでは、十分に緩冷却化の効果を得ることができないため、チル晶の生成率が5%を越え、微粉末を生成して歩留まりを低下させる問題があるほか、磁石特性もこの発明の実施例に比較して劣ることが明らかである。

【0045】

【表1】

| (at%) | | | | | | |
|-------|------|----|-----|-----|----|---|
| 合金名 | Nd | Pr | Dy | Fe | Co | B |
| 合金1 | 14.5 | 0 | 0 | bal | 0 | 6 |
| 合金2 | 9.0 | 3 | 2.5 | bal | 0 | 6 |
| 合金3 | 14.5 | 0 | 0 | bal | 3 | 6 |

【0046】

30 【表2】

| 区分 | ロール名 | 表面改質の種類 | 厚み(mm) |
|-------|-------|--------------------------------------------|---------------------|
| 本発明1 | ロール1 | Niメッキ | 1 |
| 本発明2 | ロール2 | Niメッキ | 2.5 |
| 本発明3 | ロール3 | Niメッキ | 5 |
| 本発明4 | ロール4 | Mo溶射 | 2.5 |
| 本発明5 | ロール5 | Niメッキ アルミナ溶射 | 0.5(下地) 0.5(最表面) |
| 本発明6 | ロール6 | Niメッキ TiN溶射 | 0.5(下地) 1.0(最表面) |
| 本発明7 | ロール7 | WC-17Co溶射 | 3 |
| 本発明8 | ロール8 | W-Cu溶射 | 3 |
| 本発明9 | ロール9 | Niメッキ SiC溶射 | 0.5(下地) 2(最表面) |
| 本発明10 | ロール10 | Niメッキ AlN溶射 | 0.5(下地) 2(最表面) |
| 本発明11 | ロール11 | Fe-Ni-Cu溶射 | 4 |
| 本発明12 | ロール12 | Niメッキ Si ₃ N ₄ 溶射 | 0.5(下地) 1(最表面) |
| 本発明13 | ロール13 | Niメッキ ジルコニア溶射 | 0.5(下地) 1(最表面) |
| 本発明14 | ロール14 | SiC-Ni複合溶射 溶射後HIPにより緻密化処理 | 3 |
| 比較例1 | ロール15 | 表面改質なし(銅ベリリウム合金のまま) | |
| 比較例2 | ロール16 | Crメッキ | 0.05 |

[0047]

【表3】

| ロール | 合金 | チル晶平均 生成率(%) | 柱状晶平均 一次アーム 間隔(μm) | 微粉末 生成率 (%) | 磁石特性 | | |
|-------|-----|-----------------|--------------------------|-------------------|----------|-----------------------------|------------|
| | | | | | Br kG | (BH) _{max} MGOe | iHc kOe |
| ロール1 | 合金1 | 2.0 | 3.2 | 0.5 | 14.1 | 48.7 | 12.8 |
| ロール2 | 合金1 | 0.8 | 5.0 | 0.2 | 14.2 | 49.4 | 12.5 |
| ロール3 | 合金1 | 0.3 | 6.1 | 0.1 | 14.3 | 50.1 | 12.3 |
| ロール4 | 合金1 | 0.5 | 4.8 | 0.2 | 14.2 | 49.3 | 12.5 |
| ロール5 | 合金1 | 0.2 | 7.0 | 0.1 | 14.2 | 49.2 | 12.4 |
| ロール6 | 合金1 | 0.2 | 6.2 | 0.1 | 14.3 | 49.9 | 12.2 |
| ロール7 | 合金1 | 1.3 | 4.2 | 0.4 | 14.1 | 48.6 | 13.0 |
| ロール8 | 合金1 | 1.5 | 5.1 | 0.4 | 14.1 | 48.6 | 12.6 |
| ロール9 | 合金1 | 0.8 | 6.1 | 0.2 | 14.2 | 49.1 | 12.2 |
| ロール10 | 合金1 | 0.7 | 5.9 | 0.2 | 14.2 | 49.3 | 12.6 |
| ロール11 | 合金1 | 1.2 | 3.8 | 0.3 | 14.1 | 48.7 | 13.0 |
| ロール12 | 合金1 | 0.4 | 6.2 | 0.1 | 14.3 | 50.2 | 12.2 |
| ロール13 | 合金1 | 0.5 | 6.0 | 0.2 | 14.3 | 50.0 | 12.4 |
| ロール14 | 合金1 | 1.0 | 6.3 | 0.3 | 14.1 | 48.5 | 12.8 |
| ロール2 | 合金2 | 0.6 | 4.1 | 0.2 | 12.7 | 39.4 | 23.2 |
| ロール2 | 合金3 | 0.8 | 5.5 | 0.2 | 14.2 | 49.2 | 12.6 |

【0048】

【表4】

| ロール | 合金 | チル晶平均 生成率(%) | 柱状晶平均 一次アーム 間隔(μm) | 微粉末 生成率 (%) | 磁石特性 | | |
|-------|-----|-----------------|--------------------------|-------------------|----------|-----------------|------------|
| | | | | | Br kG | (BH)max MGOe | iHc kOe |
| ロール15 | 合金1 | 9.2 | 6.1 | 1.9 | 13.6 | 45.3 | 11.7 |
| ロール15 | 合金2 | 14.3 | 3.8 | 2.8 | 12.2 | 36.4 | 21.9 |
| ロール16 | 合金3 | 10.1 | 4.9 | 1.7 | 13.5 | 44.8 | 11.4 |
| ロール16 | 合金1 | 7.6 | 5.5 | 1.7 | 13.5 | 45.0 | 11.5 |

【0049】

【表5】

| | ロール名 | 表面改質の種類 | 厚み (mm) |
|---|-------|------------------------------------------------------------------------------------------------|---------------------|
| 本 | ロール17 | Ni-50Cr溶射(wt%) | 2.5 |
| | ロール18 | Co-25Cr-12Al-0.5Y溶射(wt%) | 2.5 |
| | ロール19 | Co-32Ni-21Cr-8Al-0.5Y溶射(wt%) | 2.5 |
| | ロール20 | Ni-22Cr-10Al-1Y溶射(wt%) | 2.5 |
| | ロール21 | Co-25Cr-4W-3Fe-1C溶射(wt%) | 2.5 |
| | ロール22 | Co-28Mo-17Cr-3Si溶射(wt%) | 2.5 |
| | ロール23 | WC-12Co溶射(wt%) | 1.0 |
| | ロール24 | WC-17Co溶射(wt%) | 1.0 |
| | ロール25 | WC-27Co溶射(wt%) | 1.0 |
| | ロール26 | WC-27NiCr溶射(wt%) | 1.0 |
| 突 | ロール27 | Niメッキ Al ₂ O ₃ -3TiO ₂ 溶射(wt%) | 0.5(下地) 0.5(最表面) |
| | ロール28 | Niメッキ Al ₂ O ₃ -25ZrO ₂ -2TiO ₂ 溶射(wt%) | 0.5(下地) 0.5(最表面) |
| | ロール29 | Niメッキ Al ₂ O ₃ -22Si溶射(wt%) | 0.5(下地) 0.5(最表面) |
| | ロール30 | Niメッキ ZrO ₂ -8Y ₂ O ₃ 溶射(wt%) | 0.5(下地) 0.5(最表面) |
| | ロール31 | Niメッキ ZrO ₂ -25MgO溶射(wt%) | 0.5(下地) 0.5(最表面) |
| | ロール32 | WC-14CoCr溶射(wt%) | 0.2 |
| | ロール33 | Cr ₃ C ₂ -25NiCr溶射(wt%) | 0.2 |
| | ロール34 | Niメッキ NiCr-40Cr-40Y ₂ O ₃ | 0.5(下地) 0.2(最表面) |
| | ロール35 | Niメッキ Co-32Ni-21Cr-8Al-0.5Y-40ZrO ₂ - 40Y ₂ O ₃ 溶射(wt%) | 0.5(下地) 0.2(最表面) |
| | ロール36 | Niメッキ ZrO ₂ -33SiO ₂ 溶射(wt%) | 0.5(下地) 0.2(最表面) |
| 明 | ロール37 | Niメッキ Cr ₃ C ₂ 溶射(wt%) | 0.5(下地) 0.2(最表面) |
| | ロール38 | Niメッキ TiC溶射(wt%) | 0.5(下地) 0.2(最表面) |
| | ロール39 | Niメッキ ZrC溶射(wt%) | 0.5(下地) 0.2(最表面) |
| | ロール40 | Niメッキ ZrB ₂ 溶射(wt%) | 0.5(下地) 0.2(最表面) |

【0050】

【表6】

| | ロール名 | 合金 | チル晶 平均 生成 率(%) | 柱状晶 の平均 1次アーム 間隔(μm) | 微粉末 生成 率(%) | 磁石特性 | | |
|-------------|-------|-----|-------------------------|-------------------------------|-------------------|------------|-------------------------------|--------------|
| | | | | | | Br (kG) | (BH) _{max} (MGoe) | iHc (kOe) |
| 本 発 明 | ロール17 | 合金1 | 0.8 | 5.1 | 0.2 | 14.1 | 49.5 | 12.6 |
| | ロール18 | 合金1 | 0.7 | 5.2 | 0.2 | 14.1 | 49.4 | 12.5 |
| | ロール19 | 合金1 | 0.9 | 6.0 | 0.2 | 14.0 | 49.5 | 12.6 |
| | ロール20 | 合金1 | 0.7 | 5.1 | 0.2 | 14.2 | 49.5 | 12.4 |
| | ロール21 | 合金1 | 0.8 | 5.0 | 0.2 | 14.0 | 49.3 | 12.5 |
| | ロール22 | 合金1 | 0.7 | 5.2 | 0.1 | 14.1 | 49.4 | 12.5 |
| | ロール23 | 合金1 | 1.2 | 4.7 | 0.3 | 14.1 | 49.5 | 12.6 |
| | ロール24 | 合金1 | 1.0 | 4.5 | 0.2 | 14.2 | 49.8 | 12.7 |
| | ロール25 | 合金1 | 0.9 | 4.4 | 0.2 | 14.2 | 49.9 | 12.8 |
| | ロール26 | 合金1 | 0.9 | 4.5 | 0.2 | 14.1 | 49.7 | 12.7 |
| | ロール27 | 合金1 | 0.5 | 5.3 | 0.1 | 14.0 | 49.8 | 12.6 |
| | ロール28 | 合金1 | 0.4 | 5.3 | 0.1 | 14.0 | 49.7 | 12.5 |
| | ロール29 | 合金1 | 0.5 | 5.2 | 0.2 | 14.1 | 49.8 | 12.6 |
| | ロール30 | 合金1 | 0.4 | 5.3 | 0.1 | 14.2 | 49.8 | 12.6 |
| | ロール31 | 合金1 | 0.6 | 5.1 | 0.2 | 14.0 | 49.9 | 12.7 |
| | ロール32 | 合金1 | 1.0 | 4.4 | 0.2 | 14.1 | 49.7 | 12.7 |
| | ロール33 | 合金1 | 1.1 | 4.2 | 0.2 | 14.1 | 49.6 | 12.6 |
| | ロール34 | 合金1 | 0.9 | 4.7 | 0.2 | 14.0 | 49.6 | 12.4 |
| | ロール35 | 合金1 | 0.9 | 4.6 | 0.2 | 14.2 | 49.7 | 12.4 |
| | ロール36 | 合金1 | 0.8 | 4.7 | 0.1 | 14.1 | 49.5 | 12.3 |
| | ロール37 | 合金1 | 0.9 | 4.9 | 0.2 | 14.1 | 49.2 | 12.2 |
| | ロール38 | 合金1 | 0.9 | 4.8 | 0.2 | 14.0 | 49.3 | 12.3 |
| | ロール39 | 合金1 | 0.8 | 4.5 | 0.2 | 14.2 | 49.7 | 12.6 |
| | ロール40 | 合金1 | 0.7 | 4.9 | 0.1 | 14.1 | 49.2 | 12.3 |

【0051】

【発明の効果】この発明は、冷却用ロールを用いた急冷凝固法により製造される種々組成のR-T-B系磁石用原料合金の製造に際し、ロール表面に基材よりも熱伝導率の小さな材料による特定厚みの表面層を設けて緩冷却を図ることにより、微細なチル晶組織の生成を抑制でき、その結果、粉砕工程での微粉末の生成を防止して良好な粒度分布の成形用粉末を得ることを可能にした。さらに、その成形用粉末を用いて成形、焼結、時効熱処理を施すことにより、磁石特性の良好なR-T-B系磁石を提供することを可能とした。

【図面の簡単な説明】

【図1】単ロールによるR-T-B系磁石用原料合金の断面偏光顕微鏡組織図である。

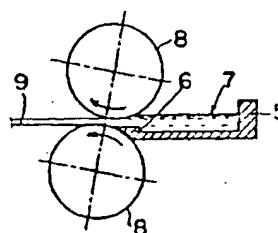
【図2】単ロールによるR-T-B系磁石用原料合金の断面偏光顕微鏡組織図であり、図1の続きである。

【図3】双ロール急冷装置を模式的に示す説明図である。

【符号の説明】

- 1 ロール面側
- 2 自由表面側
- 3 チル晶組織
- 4 柱状晶組織
- 5 タンディッシュ
- 6 タンディッシュ堰
- 7 湯面
- 8 急冷ロール
- 9 急冷凝固铸片

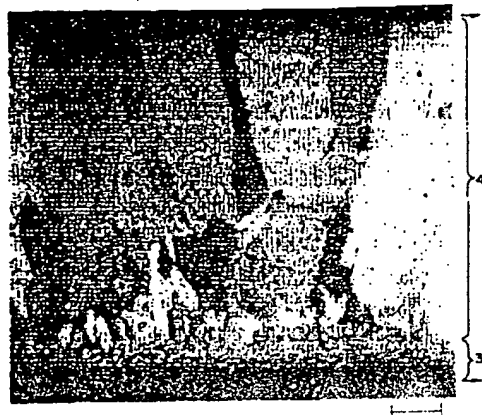
【図3】



【図1】



【図2】



フロントページの続き

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(54) RAW MATERIAL ALLOY FOR RARE EARTH MAGNET AND ITS PRODUCTION

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a raw material powder for magnet excellent in a magnetic property by forming a low heat conduction layer on a roll surface so as to suppress the generation of a fine chill crystal structure in a solidified raw material for magnet when producing a raw material for a R-T-B magnet by a rapid solidifying method by using a cooling roll.

SOLUTION: When producing a raw material for a R-T-B magnet, a molten metal of the alloy is rapidly cooled/solidified in an inert gas atmosphere of Ar, etc., or a vacuum with a twin roll method, etc., to be pulverized. In this case, a surface layer of 0.1-10 mm thickness, which is made of a material having a low coefficient of heat conduction of Ni, Cr, alumina, etc., is formed on a surface of a rapid cooling roll, which made of a material having a good coefficient of heat conduction of Cu, etc. Due to presence of the surface layer, the generation of a fine chill crystal is suppressed to a structure of the R-T-B alloy to be cooled/solidified. By setting its generation rate to $\leq 5\%$, a magnetic property of the R-T-B magnet, which is obtained by crushing the alloy and forming/sintering, is improved.

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CLAIMS

[Claim(s)]

[Claim 1] The raw material alloy for rare earth system magnets whose rate of surface ratio (average generation ratio a chill crystal organization) occupied in the whole cross-section organization of the detailed chill crystal organization which generates near the thin band front face in contact with the roll side of this raw material alloy it is the raw material alloy for R-T-B system magnets manufactured by the rapid solidification method using the roll for cooling, and is 5% or less.

[Claim 2] The manufacture approach of the raw material alloy for rare earth system magnets which forms in the molten metal cooling surface of the roll for cooling the surface layer which consists of an ingredient with thermal conductivity smaller than a roll base material by the thickness exceeding at least 0.1mm in the manufacture approach of the raw material alloy for rare earth system magnets of carrying out the rapid solidification of the R-T-B system alloy molten metal with the roll for cooling, and obtaining an alloy thin band, and performs and carries out the rapid solidification the gradual-cooling-izing by the different material surface layer.

[Claim 3] The manufacture approach of the raw material alloy for rare earth system magnets which surface layer thickness exceeds 0.1mm in claim 2, and is 10mm or less.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] Manufacture of the raw material alloy for R-T-B system magnets of a presentation is started variously. this invention is manufactured by the rapid solidification method which used the roll for cooling -- The surface layer of the specific thickness by the ingredient with thermal conductivity smaller than a base material is prepared and gradual-cooling-ized to a roll surface. By making the rate of occupying the amount of a detailed chill crystal organization generated near the roll side side front face of the alloy flake obtained in the thickness cross section of the alloy flake of a detailed chill crystal organization few, with 5% or less The detailed powder generated at the time of pulverizing of an alloy flake is decreased, and it is related with the raw material alloy for rare earth system magnets which enabled manufacture of the alloy powder for magnets which consists of predetermined particle size distribution and can expect improvement in magnetic properties, and its manufacture approach.

[0002]

[Description of the Prior Art] In recent years, the Nd-Fe-B system sintered magnet which is a highly efficient (rare earth R) system sintered magnet is used in various fields. For example, while beginning the motor built into the interior of electronic equipment, such as a hard disk drive unit, and expanding the need to a field generation source of medical equipment like nuclear-magnetic-resonance tomographic equipment (MRI) etc., the demand of the further high-performance-izing is also growing. In this background, some proposals are made about the raw material alloy by the manufacturing technology of a raw material alloy and it aiming at improvement in a magnet property.

[0003] Although the ingot which cast the molten metal to mold was ground and sintered at the beginning and the magnet was manufactured, in the ingot periphery section and a core, there was a problem of that organizations differ remarkably, crystal grain's being big and rough, and big and rough Fe depositing. When it magnet-izes using the raw material alloy which ground and obtained the casting ingot, while the rare earth elements between magnet particles in a magnet particle have inconvenient maldistribution and degrading a magnet property, a degree of sintering, a grindability, and the raw material yield were worsened also in respect of manufacture.

[0004] Some proposals about the rapid solidification method using the quenching roll as a solution over this problem are made. It is supposed that a magnet with the coercive force which was excellent in JP,60-89546,A by obtaining a tetragonal organization 5 micrometers or less by quenching can be manufactured. Moreover, in JP,63-317643,A, the manufacture approach which specified the diameter of columnar crystal grain of the raw material alloy obtained using a quenching roll and casting board thickness, and attained high performance-ization of the magnet obtained is proposed.

[0005] The manufacture approach which was going to specify manufacture conditions with a quenching roll, i.e., a cooling rate, the degree of undercooling, the cooling direction, etc., and was going to obtain proper columnar structure is proposed by JP,5-222488,A, JP,5-295490,A, and JP,7-66022,A.

[0006] Furthermore, in JP,4-55042,A and JP,5-135919,A, while covering Cr deposit with 10-100 micrometers in the roll periphery section and improving the endurance of a roll, the manufacture approach which it was going to make the proper diameter of crystal grain easier to obtain is proposed.

[0007]

[Problem(s) to be Solved by the Invention] On the other hand, also when a casting ingot is ground and obtained and considering improvement in the magnetic properties of a R-T-B system sintered magnet it uses the raw material alloy which ground the thin band alloy obtained using a quenching roll, a magnet property is worsened according to that it is easy to oxidize the detailed powder with a particle size of 1 micrometer or less generated at the time of grinding being smaller than the diameter of crystal grain again, and bringing about the fall of the raw material yield is pointed out.

[0008] Although each raw material alloy for R-T-B system magnets manufactured by the rapid solidification method using the above-mentioned roll for cooling could attain magnetic high performance-ization, it was what cannot prevent generating of detailed powder with a particle size of 1 micrometer or less at the time of grinding. Although removal of detailed powder is needed for improvement in the further magnet property, it is not easy and the raw material alloy with little generating of detailed powder is called for at the time of grinding.

[0009] This invention aims at offering that manufacture approach in the raw material alloy list concerned which can reduce generating of detailed powder with a particle size of 1 micrometer or less in the raw material alloy for R-T-B system magnets manufactured by the rapid solidification method which used the roll for cooling at the time of that grinding.

[0010]

[Means for Solving the Problem] In order that artificers may solve generating of detailed powder with a particle size [at the time of grinding of the rare earth system thin band alloy by the rapid solidification method] of 1 micrometer or less. As a result of investigating the quenching solidification structure of the raw material alloy for R-T-B system magnets, at the time of a grinding process as a factor of detailed powder generating it is shown in the side which mainly contacts the roll of the piece of casting at drawing 1 and drawing 2 at the time of quenching by roll quenching -- it needs -- etc. -- a shaft -- the knowledge of the detailed chill crystal organization being generated and this detailed chill crystal generating detailed powder in a grinding process was carried out.

[0011] Then, artificers completed this invention paying attention to the following point of 1-9, as a result of repeatedly examining variously, in order to aim at generation prevention of a detailed chill crystal organization generated at the side in contact with the roll which caused detailed powder generating at the time of grinding.

[0012] 1) The quality of the material of the cooling roller generally used conventionally is a pure copper or a copper alloy near this, and is high. [of thermal conductivity]

2) Among the cross-section solidification structure of a cast piece, in the field near the roll surface, since the cooling rate at the time of coagulation is large, a degree of undercooling is also large and the nucleation rate of coagulation is large.

3) In the large roll side close-attendants side field of a nucleation rate, it is easy to generate a detailed chill crystal organization among the cross-section organizations of a rapid solidification cast piece.

4) In order to prevent generation of a detailed chill crystal organization, it is effective to change the quality of the material in the cooling surface of a roll into the quality of the material with low thermal conductivity as compared with copper or a copper alloy.

5) It is not desirable from a viewpoint of the cooling effectiveness of the roll by water cooling to, change uniformly all the quality of the materials of the roll for cooling itself into what has low thermal conductivity on the other hand.

6) Gradual-cooling-izing by surface treatment changes only the quality of the material of the surface part of a copper roll into the quality of the material with low thermal conductivity namely, is effective there.

7) In the solidification structure of the rare earth system magnet raw material alloy manufactured by the approach of the yield of a chill crystal is low and is generating the uniform columnar crystal organization toward a free-surface side from the roll side side.

8) Generation of impalpable powder is controlled by the approach of 6, and the yield in a grinding process is improved and uniform particle size distribution are acquired.

9) The sintered magnet sintered [grinds the raw material alloy for rare earth system magnets manufactured by the approach of 6, casts, and] and obtained has good magnetic properties.

[0013] That is, this invention is a raw material alloy for R-T-B system magnets manufactured by the rapid solidification method which used the roll for cooling, and is a raw material alloy for rare earth system magnets whose rate of surface ratio (average generation ratio of a chill crystal organization) occupied in the whole cross-section organization of the detailed chill crystal organization which generates near the thin band front face in contact with the roll side of this raw material alloy is 5% or less.

[0014] Moreover, this invention is the manufacture approach of the raw material alloy for rare-earth system magnets which forms in the molten metal cooling surface of the roll for cooling the surface layer which consists of an ingredient with thermal conductivity smaller than a roll base material by the thickness exceeding at least 0.1mm, and performs carrying out the rapid solidification of the gradual-cooling-izing by the different-material surface layer in the manufacture approach of the raw material alloy for rare-earth system magnets of carrying out the rapid solidification of the R-T-B system alloy molten metal with the roll for cooling, and obtaining an alloy thin band.

[0015]

[Embodiment of the Invention] The presentation of the raw material alloy for R-T-B system magnets manufactured by

this invention uses rare earth elements (R), a transition-metals element (T), and B as a principal component, and is constituted by the unescapable impurity element on the various alloying elements selected suitably and other ingots. This is for making it constitute that it is also at 2 of R rich phase which was rich in R which plays the role which segregates to the main magnetism phase and grain boundary of ***** which consist of an atomic ratio of R₂T₁₄B₁ which shows the magnetic properties which were excellent in the permanent magnet by this invention, and promotes liquid phase sintering in a sintering process phases.

[0016] Specifically R may use Nd as a principal component, and may contain rare earth elements, such as Pr and Dy and the presentation range (sum total of R) has desirable ten atoms % - 30 atom %. 30 atom % Coercive force (IHc) sufficient by under 10 atom % is not acquired, and it is because sufficient residual magnetic flux density (Br) will not be obtained if it exceeds. The still more desirable range of R is 12 to 15 atom %.

[0017] T may specifically use Fe as a principal component, Co may be contained, and the presentation range is 42 atoms % - 88 atom %. 88 atom % It is not obtained in residual magnetic flux density sufficient by under 42 atom %, and is because sufficient coercive force will not be acquired if it exceeds. The still more desirable range of T is 77 to atom %. The permutation by Co is effective for the thermal resistance of a permanent magnet, and corrosion-resistance improvement.

[0018] The presentation range of B is two atoms % - 28 atom %. 28 atom % Coercive force sufficient by under 2 atom % is not acquired, and it is because sufficient residual magnetic flux density Br will not be obtained if it exceeds. The still more desirable range of T is four to 8 atom %.

[0019] Into furthermore, the R-Fe-B alloy containing said R and B, Fe alloy, or Co aluminum below 9.5 atom %, Ti below 4.5 atom %, V below 9.5 atom %, Cr below 8.5 atom %, Mn below 8.0 atom %, Bi below pentatomic %, Nb below 12.5 atom %, Ta below 10.5 atom %, Mo below 9.5 atom %, The high coercive force of a permanent magnet alloy becomes possible by carrying out at least one-sort addition content among W below 9.5 atom %, Sb below 2.5 atom %, germanium below 7 atom %, Sn below 3.5 atom %, Zr below 5.5 atom %, and Hf below 5.5 atom %. In the Fe-B system permanent magnet of this invention, as for a crystal layer, it is indispensable that a main stratum is ***** , and it is effective for obtaining detailed and uniform alloy powder and producing especially, the sintering permanent magnet which has outstanding magnetic properties.

[0020] This invention is characterized by facing carrying out the rapid solidification of the alloy molten metal blends so that it might become an above-mentioned presentation using a quenching roll according to a conventional method into an inert atmosphere like Ar gas, or a vacuum, and manufacturing the raw material alloy for R-T-B system magnet and attaining gradual-cooling-ization by carrying out surface treatment of the molten metal contact surface of the roll for cooling especially. The reason is for controlling generation of the detailed chill crystal organization which becomes the factor which generates impalpable powder in a next grinding process.

[0021] namely, -- although an ingredient with high thermal conductivity like copper or a copper alloy is used for the body of a quenching roll in many cases, the cooling effect of a molten metal is excessive -- becoming -- the roll side close-attendants side of a cast piece -- homaxial -- although it is easy to generate a detailed chill crystal organization can do [controlling generation of a detailed chill crystal, or] by giving surface treatment as an ingredient with thermal conductivity lower than material of roll is also to the front face of a roll.

[0022] As an ingredient of the surface layer of the roll for cooling, nickel, Mo, Cr, WC-Co, An alumina, TiN, SiC and AlN, Si₃N₄, a zirconia, nickel-50Cr, Co-23Cr-12aluminum-0.5Y, Co-32nickel-21Cr-8aluminum-0.5upsilon, nickel-22Cr-10aluminum-1Y, Co-28Cr-4W-3Fe-1C, Co-28Mo-17Cr-3Si, WC-27NiCr, aluminum₂O₃-3TiO₂, aluminum₂O₃-25ZrO₂-2TiO₂, Al₂O₃-22Si, It is effective, and, of course, ZrO₂-8Y₂O₃, ZrO₂-25MgO, WC-14CoCr, and Cr₃C₂-25NiCr, ZrO₂-33SiO₂, Cr₃C₂, and TiC, ZrC and ZrB₂ may carry out the laminating of these quality of the materials and they may use complexly. The reason with these effective quality of the materials is that the effectiveness of gradual-cooling-izing is easy to be acquired since thermal conductivity is low as compared with the alloy with which any quality of the material uses copper, such as copper and copper beryllium, as a principal component.

[0023] To the surface treatment by nickel and/or Cr, plating is desirable. Moreover, Mo, WC-Co, an alumina, TiN, SiC and AlN, Si₃N₄, a zirconia, nickel-50Cr and Co-23Cr-12aluminum-0.5Y, Co-32nickel-21Cr-8aluminum-0.5upsilon, nickel-22Cr-10aluminum-1Y, Co-28Cr-4W-3Fe-1C, Co-28Mo-17Cr-3Si, WC-27NiCr, aluminum₂O₃-3TiO₂, aluminum₂O₃-25ZrO₂-2TiO₂, Al₂O₃-22Si, To ZrO₂-8Y₂O₃, ZrO₂-25MgO, WC-14CoCr, and Cr₃C₂-25NiCr, ZrO₂-33SiO₂, Cr₃C₂, and the surface treatment by TiC, ZrC, and ZrB₂, thermal spraying is desirable. Since it excels in adhesion with the quality of the material with the body of a roll, the reason is because heat transfer is good.

[0024] Moreover, these surface layers may be used complexly. For example, independently nickel, Mo, or Cr to a roll side namely, after plating complexly, [or] Furthermore on the front face, WC-Co, an alumina, TiN, SiC, AlN, Si₃N₄ zirconia, nickel-50Cr, and Co-23Cr-12aluminum-0.5Y, Co-32nickel-21Cr-8aluminum-0.5Y, nickel-22Cr-10aluminum

1Y, Co-28Cr-4W-3Fe-1C, Co-28Mo-17Cr-3Si, WC-27NiCr, aluminum2O3-3TiO2, aluminum2O3-25ZrO2-2TiO2, aluminum2O3-22Si, Thermal spraying of ZrO 2-8upsilon2O3, ZrO2-25MgO, WC-14CoCr, and Cr3C2-25NiCr, ZrO 33SiO2, Cr3C2, and TiC, ZrC and ZrB2 may be carried out independently complexly. Moreover, metaled composite spraying is also effective. For example, composite spraying of W-Cu and Fe-nickel-Cu may be carried out, respectively. Furthermore, composite spraying of a metal and the ceramics may be given. For example, it is desirable carry out composite spraying of SiC and the nickel using a double torch, and to give a hot isostatic press (Hot Isostat Pressing; HIP) as eburnation processing after thermal spraying in this case.

[0025] As thickness of the surface layer of the roll for cooling, the range of 0.1mm or more and 10mm or less is desirable. It is to be fully unable to realize garadual-cooling-ization of an alloy cast piece in 0.1mm or less, but for a chill crystal to generate. If it exceeds 10mm, the problem to which coercive force falls when it manufactures to a permanent magnet since big-and-rough-izing of solidification structure is remarkable is produced, in order that garadual-cooling-ization may pass further, gamma-Fe of a primary phase crystallizes, an alpha-Fe phase remains in a raw material alloy by the phase transformation after coagulation, and grinding property ***** invites the fall of a magnet property and is not desirable. From this viewpoint, the still more desirable thickness range of a surface layer nickel, Mo, W-Cu, Fe-nickel-Cu, nickel-50Cr, and Co-23Cr-12aluminum-0.5Y, Co-32nickel-21Cr-8aluminum-0.5Y nickel-22Cr-10aluminum-1Y, In the case of Co-28Cr-4W-3Fe-1C and Co-28Mo-17Cr-3Si, 0.5mm, An alumina, TiN, SiC and AlN, Si3N4, a zirconia, aluminum2O3-3TiO2, aluminum2O3-25ZrO2-2TiO2, aluminum2O3-22Si, ZrO 2-8Y2O3, ZrO2-25MgO, WC-14CoCr, and Cr3C2-25NiCr, ZrO2-33SiO2, Cr3C2, and in the case of TiC, ZrC, and ZrB2, in 0.1-2mm, WC-Co, and WC-27NiCr, it is 0.5-4mm.

[0026] Although the raw material alloy for rare earth magnets of this invention is manufactured using the roll for cooling which gave the above-mentioned surface layer, that gestalt is good also by the congruence rolling method al in the single rolling method. Since it goes on from the both sides of the coagulation cast piece of a molten metal, you can make it form a uniform columnar crystal organization more thickly, in using a congruence roll especially. Consequently, there is an advantage that the manufacture effectiveness of a raw material alloy improves, and a grind property and a magnet property improve.

[0027] You may be any of the horizontal **** method which in the case of the congruence rolling method pour a top and use law or tundish about the supply approach of a molten metal. Although not limited especially about the size o roll, from a viewpoint of manufacture effectiveness and the cooling effectiveness by internal water cooling, a path is 200mm - 700mm, and it is desirable for width of face to be 200mm - 1000mm.

[0028] The raw material alloy for R-T-B system magnets manufactured by the strip casting method using the roll for cooling of this above-mentioned invention has the columnar crystal organization in which the yield of a chill crystal low and uniform. The average generation ratio of the chill crystal organization 3 generated on about one roll side sid front face is 5% or less in the surface ratio in a cross-section organization, and, specifically, the raw material alloy fo R-T-B system magnets of this invention is characterized by having the columnar crystal organization 4 where the remainder is uniform, as shown in drawing 1 and drawing 2 . An average generation ratio is 2% or less still more desirably.

[0029] Here, in this invention, a definition is given as follows and the average generation ratio of a chill crystal organization is judged. First, as a sample for organization observation, an observation side is made to detect the longitudinal-section organization of the raw material alloy for R-T-B system magnets, and it gazes at it by 500 times using a polarization microscope. A raw material alloy is embedded to resin etc., is ground in detection of an organization, and it does not take detection especially according to etching fluid etc., using as it is what finished the longitudinal section in the shape of a mirror plane by finishing buffing. The reflection electron image of a scanning electron microscope may be used for observation. A polarization image or a reflection electron image is used for making a chill crystal organization detect vividly.

[0030] The visual field to observe chooses the cross-section organization by the side of roll side close attendants at random, and takes a longitudinal-section 400 continuousmm [like drawing 1 and drawing 2] (with 500 times) organization photograph. To coincidence, the organization photograph is taken for the about 50-time low scale facto and it asks for the gross area of the raw material alloy corresponding to the field observed previously. Next, it consid as the generation ratio of a chill crystal organization with a ratio with the gross area for which asked for the area of th field which presents the chill crystal organization 3, and it asked previously in the organization photograph taken by 500 times. By such approach, it asks for the generation ratio of a chill crystal about a total of ten cross-section organization photographic strips extracted at random, and considers as the average generation ratio of a chill crystal organization.

[0031] Moreover, although primary dendrite arm spacing of a columnar crystal is usually made into the particle size

particle size of the direction of a minor axis) of a columnar crystal, a uniform columnar crystal organization is that primary [an average of] dendrite arm spacing of a columnar crystal organization is set to 3-10 micrometers. Primary dendrite arm spacing is defined as follows, and is judged here. First, as a sample for organization observation, an observation side is made to detect the longitudinal-section organization of the raw material alloy for R-T-B system magnets, and it gazes at it by 200 times using the usual optical microscope. A raw material alloy is embedded to resi etc., is ground in detection of an organization, and it does not take detection especially according to etching fluid etc using as it is what finished the longitudinal section in the shape of a mirror plane by finishing buffing.

[0032] The visual field to observe chooses ten visual fields of cross-section organizations by the side of roll side clos attendants at random, and takes a longitudinal-section organization photograph by 200 times. In these cross-section organization photographs, a straight line is drawn in location of 20mm (photograph top absolute size) from a roll sid side, and the number of the primary arms which cross the straight line is counted. It ** by the number which counted the sample absolute size equivalent to the die length of the straight line, and considers as primary dendrite arm spacin

[0033] In order to obtain the raw material alloy for R-T-B system magnets which has an above-mentioned alloy organization, it is desirable for the thickness of a cast piece to be 0.1-10mm. In less than 0.1mm, the cooling effect becomes excessive, and the generation ratio of a chill crystal exceeds 5%, the cooling effect is not fully demonstrated in 10mm or more, but there is a problem which causes big-and-rough-izing of solidification structure and generation alpha-Fe. From the viewpoint, the thickness of a still more desirable cast piece is 0.2-5mm.

[0034] The raw material alloy for R-T-B system magnets manufactured by the above-mentioned approach is manufactured by the permanent magnet with a good magnet property by performing the powder metallurgy process described below, i.e., grinding, shaping among a magnetic field, sintering, and heat treatment.

[0035] It is desirable to give preliminary grinding (hydrogen grinding) by the hydrogenation-dehydrogenation to grinding. A hydrogen treating introduces hydrogen gas, after setting the raw material alloy for R-T-B system magnet to a vacua within a chamber etc., after holding it at least 5 minutes or more, it leads it to a vacuum once again, inert g such as Ar gas, permutes it if needed, and it is processed by cooling to a room temperature. Preliminary grinding is given by performing dehydrogenation treatment after a hydrogen treating. Dehydrogenation treatment is processed b cooling to a room temperature, after holding 30 minutes or more in a vacuum at 100 degrees C - 600 degrees C.

[0036] Grinding by the jet mill is given after above-mentioned preliminary grinding. Dry type or wet attritor or a bal mill may be used for grinding. The average powder grain size after grinding has desirable 2-8 micrometers. In order that a less than 2-micrometer impalpable powder particle may tend to oxidize during grinding and average grain size may reduce a magnet property, it cannot be used, but there is a problem of causing the fall of the yield as a result. Th is a problem that, as for a particle, average grain size causes the fall of coercive force in the coarse powder end of 8-micrometer ** in order to make the grain structure of a sintered magnet big and rough. From this viewpoint, a more desirable average grain size is 2-4 micrometers.

[0037] By performing a series of above-mentioned grinding processings to the raw material alloy for R-T-B system magnets of this invention, the powder which has a good particle-size-distribution property with little impalpable powder compared with the conventional material is obtained. In shaping among a magnetic field, it is filled up with t powder of the raw material alloy for R-T-B system magnets obtained by the above-mentioned approach by the mold made from austenite steel, the mold made of rubber, for example, the product, of a non-magnetic material, or martensitic steel, and after carrying out orientation of the powder particle by impressing a pulsed magnetic field, it fabricates with a press. Moreover, a static magnetic field or a pulsed magnetic field, and a static magnetic field may combined instead of a pulsed magnetic field.

[0038] Sintering is processed at 1030 degrees C - 1150 degrees C in a vacuum or Ar inert gas ambient atmosphere fo to 4 hours. The permanent magnet of this invention is manufactured by performing aging heat treatment for 30 - 90 minutes at 450 degrees C - 650 degrees C if needed after that. Moreover, the raw material alloy for magnets manufactured by this invention is possible also for application in a HDDR process, and usable also to a bond magnet [0039]

[Example]

The alloy of the presentation shown in example 1 table 1 was once decompressed to 0.01Torr(s), and it dissolved by high-frequency induction heating in the ambient atmosphere which poured in Ar gas up to gage pressure 0.2 atmospheric pressure. The rapid solidification cast piece was produced with the congruence roll quenching equipmen shown in drawing 3 using this molten metal. The surface of hot water 7 goes up gradually as drawing 3 is what show rapid solidification equipment typically, and teeming is carried out from the tundish 5 upper part, and a molten meta once accumulated in tundish 5 and carries out teeming, and it is **. It overflows from the tundish weir 6 and results roll 8. The roll 8 has rotated in the direction of the arrow head in drawing beforehand, rapid solidification is carried o

with a roll 8, and the rapid solidification cast piece 9 is produced.

[0040] The diameter of a roll shall be 600mm and the base material shall show the quality of the material of the surface layer in Table 2 and 5 using a copper beryllium alloy. Moreover, the gap during a roll was adjusted so that it might be set to 1-2mm. In addition, although this example was explained by the case where a congruence roll is used, even when a single roll was used, it was checked that the same effectiveness had been acquired.

[0041] The obtained cast piece was held in 3kg/cm² H₂ gas ambient atmosphere for 2 hours, and carried out the hydrogen treating to it, and it held at 500 degrees C among the vacuum after that for 5 hours, dehydrogenation treatment was performed, and it considered as preliminary grinding by cooling to a room temperature. About magnet field shaping, the mold made of rubber was filled up with the obtained powder, and after carrying out orientation of the powder by impressing the pulsed magnetic field of 30kOe momentarily, the hydrostatic-pressure press was given. After holding this Plastic solid in 3 hours and sintering it at 1090 degrees C, aging heat treatment of 1 hour was performed at 600 degrees C, and the permanent magnet was obtained.

[0042] As the chill crystal yield of the cast piece obtained by the approach of this invention was shown in Table 3 and 6, it was 5% or less, and primary arm spacing of a columnar crystal was set to 3.2-7 micrometers, the detailed powder yield after grinding was low, and the magnetic maximum energy product was greatly good compared with the example of a comparison.

[0043] The same trial as an example was performed using the thing with the copper beryllium alloy which is a base material, without reforming the peripheral face of an example of comparison 1 quenching roll. It is shown in Table 4 making the result into the example of a comparison. Although spacing of a primary D1N light arm was the same as that of an example, the yield of a chill crystal was over 5%, the fines yield was also high and the magnet property was also that in which a maximum energy product is small inferior as compared with an example.

[0044] The same trial as an example was performed using the quenching roll which reformed the peripheral face by plating with an example of comparison 2 thickness of 50 micrometers. The result is shown in Table 4. In Cr plating, since effectiveness of gradual-cooling-izing cannot fully be acquired, there is a problem on which the yield of a chill crystal exceeds 5%, impalpable powder is generated, and the yield is reduced, and also it is clear that a magnet property is also inferior as compared with the example of this invention.

[0045]

[Table 1]

(at%)

| 合金名 | Nd | Pr | Dy | Fe | Co | B |
|-----|------|----|-----|-----|----|---|
| 合金1 | 14.5 | 0 | 0 | bal | 0 | 6 |
| 合金2 | 9.0 | 3 | 2.5 | bal | 0 | 6 |
| 合金3 | 14.5 | 0 | 0 | bal | 3 | 6 |

[0046]

[Table 2]

| 区分 | ロール名 | 表面改質の種類 | 厚み(mm) |
|-------|-------|--------------------------------------------|---------------------|
| 本発明1 | ロール1 | Niメッキ | 1 |
| 本発明2 | ロール2 | Niメッキ | 2.5 |
| 本発明3 | ロール3 | Niメッキ | 5 |
| 本発明4 | ロール4 | Mo溶射 | 2.5 |
| 本発明5 | ロール5 | Niメッキ アルミナ溶射 | 0.5(下地) 0.5(最表面) |
| 本発明6 | ロール6 | Niメッキ TiN溶射 | 0.5(下地) 1.0(最表面) |
| 本発明7 | ロール7 | WC-17Co溶射 | 3 |
| 本発明8 | ロール8 | W-Cu溶射 | 3 |
| 本発明9 | ロール9 | Niメッキ SiC溶射 | 0.5(下地) 2(最表面) |
| 本発明10 | ロール10 | Niメッキ AlN溶射 | 0.5(下地) 2(最表面) |
| 本発明11 | ロール11 | Fe-Ni-Cu溶射 | 4 |
| 本発明12 | ロール12 | Niメッキ Si ₃ N ₄ 溶射 | 0.5(下地) 1(最表面) |
| 本発明13 | ロール13 | Niメッキ ジルコニア溶射 | 0.5(下地) 1(最表面) |
| 本発明14 | ロール14 | SiC-Ni複合溶射 溶射後HIPにより緻密化処理 | 3 |
| 比較例1 | ロール15 | 表面改質なし(銅ベリリウム合金のまま) | |
| 比較例2 | ロール16 | Crメッキ | 0.05 |

[0047]

[Table 3]

| ロール | 合金 | チル晶平均 生成率(%) | 柱状晶平均 一次アーム 間隔(μm) | 微粉末 生成率 (%) | 磁石特性 | | |
|-------|-----|-----------------|--------------------------|-------------------|----------|-----------------|------------|
| | | | | | Br kG | (BH)max MGOe | iHc kOe |
| ロール1 | 合金1 | 2.0 | 3.2 | 0.5 | 14.1 | 48.7 | 12.8 |
| ロール2 | 合金1 | 0.8 | 5.0 | 0.2 | 14.2 | 49.4 | 12.5 |
| ロール3 | 合金1 | 0.3 | 6.1 | 0.1 | 14.3 | 50.1 | 12.3 |
| ロール4 | 合金1 | 0.5 | 4.8 | 0.2 | 14.2 | 49.3 | 12.5 |
| ロール5 | 合金1 | 0.2 | 7.0 | 0.1 | 14.2 | 49.2 | 12.4 |
| ロール6 | 合金1 | 0.2 | 6.2 | 0.1 | 14.3 | 49.9 | 12.2 |
| ロール7 | 合金1 | 1.3 | 4.2 | 0.4 | 14.1 | 48.8 | 13.0 |
| ロール8 | 合金1 | 1.6 | 5.1 | 0.4 | 14.1 | 48.6 | 12.6 |
| ロール9 | 合金1 | 0.8 | 6.1 | 0.2 | 14.2 | 49.1 | 12.2 |
| ロール10 | 合金1 | 0.7 | 5.9 | 0.2 | 14.2 | 49.3 | 12.6 |
| ロール11 | 合金1 | 1.2 | 3.8 | 0.3 | 14.1 | 48.7 | 13.0 |
| ロール12 | 合金1 | 0.4 | 6.2 | 0.1 | 14.3 | 50.2 | 12.2 |
| ロール13 | 合金1 | 0.5 | 6.0 | 0.2 | 14.3 | 50.0 | 12.4 |
| ロール14 | 合金1 | 1.0 | 6.3 | 0.3 | 14.1 | 48.5 | 12.8 |
| ロール2 | 合金2 | 0.6 | 4.1 | 0.2 | 12.7 | 39.4 | 23.2 |
| ロール2 | 合金3 | 0.8 | 5.5 | 0.2 | 14.2 | 49.2 | 12.6 |

[0048]

[Table 4]

| ロール | 合金 | チル晶平均 生成率(%) | 柱状晶平均 一次アーム 間隔(μm) | 微粉末 生成率 (%) | 磁石特性 | | |
|-------|-----|-----------------|--------------------------|-------------------|----------|-----------------|------------|
| | | | | | Br kG | (BH)max MGOe | iHc kOe |
| ロール15 | 合金1 | 9.2 | 6.1 | 1.9 | 13.6 | 45.3 | 11.7 |
| ロール15 | 合金2 | 14.3 | 3.8 | 2.8 | 12.2 | 36.4 | 21.9 |
| ロール15 | 合金3 | 10.1 | 4.9 | 1.7 | 13.5 | 44.8 | 11.4 |
| ロール16 | 合金1 | 7.6 | 5.5 | 1.7 | 13.5 | 45.0 | 11.5 |

[0049]

[Table 5]

| | ロール名 | 表面改質の種類 | 厚み (mm) |
|-------------|-------|-----------------------------------------------------------------------------------|------------|
| 本 発 明 | ロール17 | Ni-50Cr溶射(wt%) | 2.5 |
| | ロール18 | Co-23Cr-12Al-0.5Y溶射(wt%) | 2.5 |
| | ロール19 | Co-32Ni-21Cr-8Al-0.5Y溶射(wt%) | 2.5 |
| | ロール20 | Ni-22Cr-10Al-1Y溶射(wt%) | 2.5 |
| | ロール21 | Co-28Cr-4W-3Fe-1C溶射(wt%) | 2.5 |
| | ロール22 | Co-28Mo-17Cr-3Si溶射(wt%) | 2.5 |
| | ロール23 | WC-12Co溶射(wt%) | 1.0 |
| | ロール24 | WC-17Co溶射(wt%) | 1.0 |
| | ロール25 | WC-27Co溶射(wt%) | 1.0 |
| | ロール26 | WC-27NiCr溶射(wt%) | 1.0 |
| | ロール27 | Niメッキ | 0.5(下地) |
| | | Al ₂ O ₃ -3TiO ₂ 溶射(wt%) | 0.5(最表面) |
| | ロール28 | Niメッキ | 0.5(下地) |
| | | Al ₂ O ₃ -25ZrO ₂ -2TiO ₂ 溶射(wt%) | 0.5(最表面) |
| | ロール29 | Niメッキ | 0.5(下地) |
| | | Al ₂ O ₃ -22Si溶射(wt%) | 0.5(最表面) |
| | ロール30 | Niメッキ | 0.5(下地) |
| | | ZrO ₂ -8Y ₂ O ₃ 溶射(wt%) | 0.5(最表面) |
| | ロール31 | Niメッキ | 0.5(下地) |
| | | ZrO ₂ -25MgO溶射(wt%) | 0.5(最表面) |
| | ロール32 | WC-14CoCr溶射(wt%) | 0.2 |
| | ロール33 | Cr ₃ C ₂ -25NiCr溶射(wt%) | 0.2 |
| | ロール34 | Niメッキ | 0.5(下地) |
| | | NiCr-40ZrO ₂ -40Y ₂ O ₃ | 0.2(最表面) |
| | ロール35 | Niメッキ | 0.5(下地) |
| | | Co-32Ni-21Cr-8Al-0.5Y-40ZrO ₂ -40Y ₂ O ₃ 溶射(wt%) | 0.2(最表面) |
| | ロール36 | Niメッキ | 0.5(下地) |
| | | ZrO ₂ -33SiO ₂ 溶射(wt%) | 0.2(最表面) |
| | ロール37 | Niメッキ | 0.5(下地) |
| | | Cr ₃ C ₂ 溶射(wt%) | 0.2(最表面) |
| | ロール38 | Niメッキ | 0.5(下地) |
| | | TiC溶射(wt%) | 0.2(最表面) |
| | ロール39 | Niメッキ | 0.5(下地) |
| | | ZrC溶射(wt%) | 0.2(最表面) |
| | ロール40 | Niメッキ | 0.5(下地) |
| | | ZrB ₂ 溶射(wt%) | 0.2(最表面) |

[0050]

[Table 6]

| | ロール名 | 合金 | チル晶 平均 生成 率(%) | 柱状晶 の平均 1次アーム 間隔(μm) | 微粉末 生成 率(%) | 磁石特性 | | |
|---|-------|-----|-------------------------|-------------------------------|-------------------|------------|-------------------------------|--------------|
| | | | | | | Br (kG) | (BH) _{max} (MGOe) | iHc (kOe) |
| 本 | ロール17 | 合金1 | 0.8 | 5.1 | 0.2 | 14.1 | 49.5 | 12.6 |
| | ロール18 | 合金1 | 0.7 | 5.2 | 0.2 | 14.1 | 49.4 | 12.5 |
| | ロール19 | 合金1 | 0.9 | 5.0 | 0.2 | 14.0 | 49.5 | 12.6 |
| | ロール20 | 合金1 | 0.7 | 5.1 | 0.2 | 14.2 | 49.5 | 12.4 |
| | ロール21 | 合金1 | 0.8 | 5.0 | 0.2 | 14.0 | 49.3 | 12.5 |
| | ロール22 | 合金1 | 0.7 | 5.2 | 0.1 | 14.1 | 49.4 | 12.5 |
| | ロール23 | 合金1 | 1.2 | 4.7 | 0.3 | 14.1 | 49.5 | 12.6 |
| | ロール24 | 合金1 | 1.0 | 4.5 | 0.2 | 14.2 | 49.8 | 12.7 |
| | ロール25 | 合金1 | 0.9 | 4.4 | 0.2 | 14.2 | 49.9 | 12.8 |
| | ロール26 | 合金1 | 0.9 | 4.5 | 0.2 | 14.1 | 49.7 | 12.7 |
| 発 | ロール27 | 合金1 | 0.5 | 5.3 | 0.1 | 14.0 | 49.8 | 12.6 |
| | ロール28 | 合金1 | 0.4 | 5.3 | 0.1 | 14.0 | 49.7 | 12.5 |
| | ロール29 | 合金1 | 0.5 | 5.2 | 0.2 | 14.1 | 49.8 | 12.6 |
| | ロール30 | 合金1 | 0.4 | 5.3 | 0.1 | 14.2 | 49.8 | 12.6 |
| | ロール31 | 合金1 | 0.6 | 5.1 | 0.2 | 14.0 | 49.9 | 12.7 |
| | ロール32 | 合金1 | 1.0 | 4.4 | 0.2 | 14.1 | 49.7 | 12.7 |
| | ロール33 | 合金1 | 1.1 | 4.2 | 0.2 | 14.1 | 49.6 | 12.6 |
| | ロール34 | 合金1 | 0.9 | 4.7 | 0.2 | 14.0 | 49.6 | 12.4 |
| | ロール35 | 合金1 | 0.9 | 4.6 | 0.2 | 14.2 | 49.7 | 12.4 |
| | ロール36 | 合金1 | 0.8 | 4.7 | 0.1 | 14.1 | 49.5 | 12.3 |
| 明 | ロール37 | 合金1 | 0.9 | 4.9 | 0.2 | 14.1 | 49.2 | 12.2 |
| | ロール38 | 合金1 | 0.9 | 4.8 | 0.2 | 14.0 | 49.3 | 12.3 |
| | ロール39 | 合金1 | 0.8 | 4.5 | 0.2 | 14.2 | 49.7 | 12.6 |
| | ロール40 | 合金1 | 0.7 | 4.9 | 0.1 | 14.1 | 49.2 | 12.3 |

[0051]

[Effect of the Invention] This invention made it possible to be able to control generation of a detailed chill crystal organization, consequently to prevent generation of the impalpable powder in a grinding process, and to obtain the powder for shaping of good particle size distribution by preparing the surface layer of the according to ingredient with thermal conductivity smaller than base material to roll surface variously on the occasion of manufacture of raw material alloy for R-T-B system magnets of presentation specification thickness manufactured by the rapid-solidification method which used the roll for cooling, and attaining gradual-cooling-ization. Furthermore, it made it possible to of a R-T-B system magnet with a good magnet property by performing shaping, sintering, and aging heat treatment using the powder for shaping.

[Translation done.]

* NOTICES *

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] Manufacture of the raw material alloy for R-T-B system magnets of a presentation is started variously. this invention is manufactured by the rapid solidification method which used the roll for cooling -- The surface layer of the specific thickness by the ingredient with thermal conductivity smaller than a base material is prepared and gradual-cooling-ized to a roll surface. By making the rate of occupying the amount of a detailed chill crystal organization generated near the roll side side front face of the alloy flake obtained in the thickness cross section of the alloy flake of a detailed chill crystal organization few, with 5% or less The detailed powder generated at the time of pulverizing of an alloy flake is decreased, and it is related with the raw material alloy for rare earth system magnets which enabled manufacture of the alloy powder for magnets which consists of predetermined particle size distribution and can expect improvement in magnetic properties, and its manufacture approach.

[0002]

[Description of the Prior Art] In recent years, the Nd-Fe-B system sintered magnet which is a highly efficient (rare earth R) system sintered magnet is used in various fields. For example, while beginning the motor built into the interior of electronic equipment, such as a hard disk drive unit, and expanding the need to a field generation source of medical equipment like nuclear-magnetic-resonance tomographic equipment (MRI) etc., the demand of the further high-performance-izing is also growing. In this background, some proposals are made about the raw material alloy by the manufacturing technology of a raw material alloy and it aiming at improvement in a magnet property.

[0003] Although the ingot which cast the molten metal to mold was ground and sintered at the beginning and the magnet was manufactured, in the ingot periphery section and a core, there was a problem of that organizations differ remarkably, crystal grain's being big and rough, and big and rough Fe depositing. When it magnet-izes using the raw material alloy which ground and obtained the casting ingot, while the rare earth elements between magnet particles in a magnet particle have inconvenient maldistribution and degrading a magnet property, a degree of sintering, a grindability, and the raw material yield were worsened also in respect of manufacture.

[0004] Some proposals about the rapid solidification method using the quenching roll as a solution over this problem are made. It is supposed that a magnet with the coercive force which was excellent in JP,60-89546,A by obtaining a tetragonal organization 5 micrometers or less by quenching can be manufactured. Moreover, in JP,63-317643,A, the manufacture approach which specified the diameter of columnar crystal grain of the raw material alloy obtained using a quenching roll and casting board thickness, and attained high performance-ization of the magnet obtained is proposed.

[0005] The manufacture approach which was going to specify manufacture conditions with a quenching roll, i.e., a cooling rate, the degree of undercooling, the cooling direction, etc., and was going to obtain proper columnar structure is proposed by JP,5-222488,A, JP,5-295490,A, and JP,7-66022,A.

[0006] Furthermore, in JP,4-55042,A and JP,5-135919,A, while covering Cr deposit with 10-100 micrometers in the roll periphery section and improving the endurance of a roll, the manufacture approach which it was going to make the proper diameter of crystal grain easier to obtain is proposed.

[0007]

[Problem(s) to be Solved by the Invention] On the other hand, also when a casting ingot is ground and obtained and considering improvement in the magnetic properties of a R-T-B system sintered magnet it uses the raw material alloy which ground the thin band alloy obtained using a quenching roll, a magnet property is worsened according to that it is easy to oxidize the detailed powder with a particle size of 1 micrometer or less generated at the time of grinding being smaller than the diameter of crystal grain again, and bringing about the fall of the raw material yield is pointed out.

[0008] Although each raw material alloy for R-T-B system magnets manufactured by the rapid solidification method using the above-mentioned roll for cooling could attain magnetic high performance-ization, it was what cannot prevent generating of detailed powder with a particle size of 1 micrometer or less at the time of grinding. Although removal of detailed powder is needed for improvement in the further magnet property, it is not easy and the raw material alloy with little generating of detailed powder is called for at the time of grinding.

[0009] This invention aims at offering that manufacture approach in the raw material alloy list concerned which can reduce generating of detailed powder with a particle size of 1 micrometer or less in the raw material alloy for R-T-B system magnets manufactured by the rapid solidification method which used the roll for cooling at the time of that grinding.

[0010]

[Means for Solving the Problem] In order that artificers may solve generating of detailed powder with a particle size [at the time of grinding of the rare earth system thin band alloy by the rapid solidification method] of 1 micrometer or less. As a result of investigating the quenching solidification structure of the raw material alloy for R-T-B system alloys, at the time of a grinding process as a factor of detailed powder generating it is shown in the side which mainly contacts the roll of the piece of casting at drawing 1 and drawing 2 at the time of quenching by roll quenching -- it needs -- etc. -- a shaft -- the knowledge of the detailed chill crystal organization being generated and this detailed chill crystal generating detailed powder in a grinding process was carried out.

[0011] Then, artificers completed this invention paying attention to the following point of 1-9, as a result of repeating examination variously, in order to aim at generation prevention of a detailed chill crystal organization generated at the side in contact with the roll which caused detailed powder generating at the time of grinding.

[0012] 1) The quality of the material of the cooling roller generally used conventionally is a pure copper or a copper alloy near this, and is high. [of thermal conductivity]

2) Among the cross-section solidification structure of a cast piece, in the field near the roll surface, since the cooling rate at the time of coagulation is large, a degree of undercooling is also large and the nucleation rate of coagulation is large.

3) In the large roll side close-attendants side field of a nucleation rate, it is easy to generate a detailed chill crystal organization among the cross-section organizations of a rapid solidification cast piece.

4) In order to prevent generation of a detailed chill crystal organization, it is effective to change the quality of the material in the cooling surface of a roll into the quality of the material with low thermal conductivity as compared with copper or a copper alloy.

5) It is not desirable from a viewpoint of the cooling effectiveness of the roll by water cooling to, change uniformly all the quality of the materials of the roll for cooling itself into what has low thermal conductivity on the other hand.

6) Gradual-cooling-izing by surface treatment changes only the quality of the material of the surface part of a copper roll into the quality of the material with low thermal conductivity namely, is effective there.

7) In the solidification structure of the rare earth system magnet raw material alloy manufactured by the approach of the yield of a chill crystal is low and is generating the uniform columnar crystal organization toward a free-surface side from the roll side side.

8) Generation of impalpable powder is controlled by the approach of 6, and the yield in a grinding process is improved and uniform particle size distribution are acquired.

9) The sintered magnet sintered [grinds the raw material alloy for rare earth system magnets manufactured by the approach of 6, casts, and] and obtained has good magnetic properties.

[0013] That is, this invention is a raw material alloy for R-T-B system magnets manufactured by the rapid solidification method which used the roll for cooling, and is a raw material alloy for rare earth system magnets whose rate of surface ratio (average generation ratio of a chill crystal organization) occupied in the whole cross-section organization of the detailed chill crystal organization which generates near the thin band front face in contact with the roll side of this raw material alloy is 5% or less.

[0014] Moreover, this invention is the manufacture approach of the raw material alloy for rare-earth system magnets which forms in the molten metal cooling surface of the roll for cooling the surface layer which consists of an ingredient with thermal conductivity smaller than a roll base material by the thickness exceeding at least 0.1mm, and performs carrying out the rapid solidification of the gradual-cooling-izing by the different-material surface layer in the manufacture approach of the raw material alloy for rare-earth system magnets of carrying out the rapid solidification of the R-T-B system alloy molten metal with the roll for cooling, and obtaining an alloy thin band.

[0015]

[Embodiment of the Invention] The presentation of the raw material alloy for R-T-B system magnets manufactured by

this invention uses rare earth elements (R), a transition-metals element (T), and B as a principal component, and is constituted by the unescapable impurity element on the various alloying elements selected suitably and other ingots. This is for making it constitute that it is also at 2 of R rich phase which was rich in R which plays the role which segregates to the main magnetism phase and grain boundary of ***** which consist of an atomic ratio of R₂T₁₄B₁ which shows the magnetic properties which were excellent in the permanent magnet by this invention, and promotes liquid phase sintering in a sintering process phases.

[0016] Specifically R may use Nd as a principal component, and may contain rare earth elements, such as Pr and Dy and the presentation range (sum total of R) has desirable ten atoms % - 30 atom %. 30 atom % Coercive force (IHc) sufficient by under 10 atom % is not acquired, and it is because sufficient residual magnetic flux density (Br) will not be obtained if it exceeds. The still more desirable range of R is 12 to 15 atom %.

[0017] T may specifically use Fe as a principal component, Co may be contained, and the presentation range is 42 atoms % - 88 atom %. 88 atom % It is not obtained in residual magnetic flux density sufficient by under 42 atom %, and is because sufficient coercive force will not be acquired if it exceeds. The still more desirable range of T is 77 to atom %. The permutation by Co is effective for the thermal resistance of a permanent magnet, and corrosion-resistance improvement.

[0018] The presentation range of B is two atoms % - 28 atom %. 28 atom % Coercive force sufficient by under 2 atom % is not acquired, and it is because sufficient residual magnetic flux density Br will not be obtained if it exceeds. The still more desirable range of T is four to 8 atom %.

[0019] Into furthermore, the R-Fe-B alloy containing said R and B, Fe alloy, or Co aluminum below 9.5 atom %, Ti below 4.5 atom %, V below 9.5 atom %, Cr below 8.5 atom %, Mn below 8.0 atom %, Bi below pentatomic %, Nb below 12.5 atom %, Ta below 10.5 atom %, Mo below 9.5 atom %, The high coercive force of a permanent magnet alloy becomes possible by carrying out at least one-sort addition content among W below 9.5 atom %, Sb below 2.5 atom %, germanium below 7 atom %, Sn below 3.5 atom %, Zr below 5.5 atom %, and Hf below 5.5 atom %. In the Fe-B system permanent magnet of this invention, as for a crystal layer, it is indispensable that a main stratum is ***** , and it is effective for obtaining detailed and uniform alloy powder and producing especially, the sintering permanent magnet which has outstanding magnetic properties.

[0020] This invention is characterized by facing carrying out the rapid solidification of the alloy molten metal blends so that it might become an above-mentioned presentation using a quenching roll according to a conventional method into an inert atmosphere like Ar gas, or a vacuum, and manufacturing the raw material alloy for R-T-B system magnet and attaining gradual-cooling-ization by carrying out surface treatment of the molten metal contact surface of the roll for cooling especially. The reason is for controlling generation of the detailed chill crystal organization which becomes the factor which generates impalpable powder in a next grinding process.

[0021] namely, -- although an ingredient with high thermal conductivity like copper or a copper alloy is used for the body of a quenching roll in many cases, the cooling effect of a molten metal is excessive -- becoming -- the roll side close-attendants side of a cast piece -- homaxial -- although it is easy to generate a detailed chill crystal organization can do [controlling generation of a detailed chill crystal, or] by giving surface treatment as an ingredient with thermal conductivity lower than material of roll is also to the front face of a roll.

[0022] As an ingredient of the surface layer of the roll for cooling, nickel, Mo, Cr, WC-Co, An alumina, TiN, SiC, AlN, Si₃N₄, a zirconia, nickel-50Cr, Co-23Cr-12aluminum-0.5Y, Co-32nickel-21Cr-8aluminum-0.5upsilon, nickel-22Cr-10aluminum-1Y, Co-28Cr-4W-3Fe-1C, Co-28Mo-17Cr-3Si, WC-27NiCr, aluminum₂O₃-3TiO₂, aluminum₂O₃-25ZrO₂-2TiO₂, Al₂O₃-22Si, It is effective, and, of course, ZrO₂-8Y₂O₃, ZrO₂-25MgO, WC-14CoCr, and Cr₃C₂-25NiCr, ZrO₂-33SiO₂, Cr₃C₂, and TiC, ZrC and ZrB₂ may carry out the laminating of these quality of the materials and they may use complexly. The reason with these effective quality of the materials is that the effectiveness of gradual-cooling-izing is easy to be acquired since thermal conductivity is low as compared with the alloy with which any quality of the material uses copper, such as copper and copper beryllium, as a principal component.

[0023] To the surface treatment by nickel and/or Cr, plating is desirable. Moreover, Mo, WC-Co, an alumina, TiN, SiC, AlN, Si₃N₄, a zirconia, nickel-50Cr and Co-23Cr-12aluminum-0.5Y, Co-32nickel-21Cr-8aluminum-0.5upsilon, nickel-22Cr-10aluminum-1Y, Co-28Cr-4W-3Fe-1C, Co-28Mo-17Cr-3Si, WC-27NiCr, aluminum₂O₃-3TiO₂, aluminum₂O₃-25ZrO₂-2TiO₂, Al₂O₃-22Si, To ZrO₂-8Y₂O₃, ZrO₂-25MgO, WC-14CoCr, and Cr₃C₂-25NiCr, ZrO₂-33SiO₂, Cr₃C₂, and the surface treatment by TiC, ZrC, and ZrB₂, thermal spraying is desirable. Since it excels in adhesion with the quality of the material with the body of a roll, the reason is because heat transfer is good.

[0024] Moreover, these surface layers may be used complexly. For example, independently nickel, Mo, or Cr to a roll side namely, after plating complexly, [or] Furthermore on the front face, WC-Co, an alumina, TiN, SiC, AlN, Si₃N₄, zirconia, nickel-50Cr, and Co-23Cr-12aluminum-0.5Y, Co-32nickel-21Cr-8aluminum-0.5Y, nickel-22Cr-10aluminum

1Y, Co-28Cr-4W-3Fe-1C, Co-28Mo-17Cr-3Si, WC-27NiCr, aluminum2O3-3TiO2, aluminum2O3-25ZrO2-2TiO2, aluminum2O3-22Si, Thermal spraying of ZrO 2-8upsilon2O3, ZrO2-25MgO, WC-14CoCr, and Cr3C2-25NiCr, ZrO 33SiO2, Cr3C2, and TiC, ZrC and ZrB2 may be carried out independently complexly. Moreover, metaled composite spraying is also effective. For example, composite spraying of W-Cu and Fe-nickel-Cu may be carried out, respectively. Furthermore, composite spraying of a metal and the ceramics may be given. For example, it is desirable carry out composite spraying of SiC and the nickel using a double torch, and to give a hot isostatic press (Hot Isostat Pressing; HIP) as eburnation processing after thermal spraying in this case.

[0025] As thickness of the surface layer of the roll for cooling, the range of 0.1mm or more and 10mm or less is desirable. It is to be fully unable to realize garadual-cooling-ization of an alloy cast piece in 0.1mm or less, but for a chill crystal to generate. If it exceeds 10mm, the problem to which coercive force falls when it manufactures to a permanent magnet since big-and-rough-izing of solidification structure is remarkable is produced, in order that garadual-cooling-ization may pass further, gamma-Fe of a primary phase crystallizes, an alpha-Fe phase remains in a raw material alloy by the phase transformation after coagulation, and grinding property ***** invites the fall of a magnet property and is not desirable. From this viewpoint, the still more desirable thickness range of a surface layer nickel, Mo, W-Cu, Fe-nickel-Cu, nickel-50Cr, and Co-23Cr-12aluminum-0.5Y, Co-32nickel-21Cr-8aluminum-0.5Y nickel-22Cr-10aluminum-1Y, In the case of Co-28Cr-4W-3Fe-1C and Co-28Mo-17Cr-3Si, 0.5mm, An alumina, TiN, SiC and AlN, Si3N4, a zirconia, aluminum2O3-3TiO2, aluminum2O3-25ZrO2-2TiO2, aluminum2O3-22Si, ZrO 2-8Y2O3, ZrO2-25MgO, WC-14CoCr, and Cr3C2-25NiCr, ZrO2-33SiO2, Cr3C2, and in the case of TiC, ZrC, and ZrB2, in 0.1-2mm, WC-Co, and WC-27NiCr, it is 0.5-4mm.

[0026] Although the raw material alloy for rare earth magnets of this invention is manufactured using the roll for cooling which gave the above-mentioned surface layer, that gestalt is good also by the congruence rolling method al in the single rolling method. Since it goes on from the both sides of the coagulation cast piece of a molten metal, you can make it form a uniform columnar crystal organization more thickly, in using a congruence roll especially. Consequently, there is an advantage that the manufacture effectiveness of a raw material alloy improves, and a grind property and a magnet property improve.

[0027] You may be any of the horizontal **** method which in the case of the congruence rolling method pour a top and use law or tundish about the supply approach of a molten metal. Although not limited especially about the size o roll, from a viewpoint of manufacture effectiveness and the cooling effectiveness by internal water cooling, a path is 200mm - 700mm, and it is desirable for width of face to be 200mm - 1000mm.

[0028] The raw material alloy for R-T-B system magnets manufactured by the strip casting method using the roll for cooling of this above-mentioned invention has the columnar crystal organization in which the yield of a chill crystal low and uniform. The average generation ratio of the chill crystal organization 3 generated on about one roll side sid front face is 5% or less in the surface ratio in a cross-section organization, and, specifically, the raw material alloy fo R-T-B system magnets of this invention is characterized by having the columnar crystal organization 4 where the remainder is uniform, as shown in drawing 1 and drawing 2 . An average generation ratio is 2% or less still more desirably.

[0029] Here, in this invention, a definition is given as follows and the average generation ratio of a chill crystal organization is judged. First, as a sample for organization observation, an observation side is made to detect the longitudinal-section organization of the raw material alloy for R-T-B system magnets, and it gazes at it by 500 times using a polarization microscope. A raw material alloy is embedded to resin etc., is ground in detection of an organization, and it does not take detection especially according to etching fluid etc., using as it is what finished the longitudinal section in the shape of a mirror plane by finishing buffing. The reflection electron image of a scanning electron microscope may be used for observation. A polarization image or a reflection electron image is used for making a chill crystal organization detect vividly.

[0030] The visual field to observe chooses the cross-section organization by the side of roll side close attendants at random, and takes a longitudinal-section 400 continuousmm [like drawing 1 and drawing 2] (with 500 times) organization photograph. To coincidence, the organization photograph is taken for the about 50-time low scale facto and it asks for the gross area of the raw material alloy corresponding to the field observed previously. Next, it consid as the generation ratio of a chill crystal organization with a ratio with the gross area for which asked for the area of th field which presents the chill crystal organization 3, and it asked previously in the organization photograph taken by 500 times. By such approach, it asks for the generation ratio of a chill crystal about a total of ten cross-section organization photographic strips extracted at random, and considers as the average generation ratio of a chill crystal organization.

[0031] Moreover, although primary dendrite arm spacing of a columnar crystal is usually made into the particle size

particle size of the direction of a minor axis) of a columnar crystal, a uniform columnar crystal organization is that primary [an average of] dendrite arm spacing of a columnar crystal organization is set to 3-10 micrometers. Primary dendrite arm spacing is defined as follows, and is judged here. First, as a sample for organization observation, an observation side is made to detect the longitudinal-section organization of the raw material alloy for R-T-B system magnets, and it gazes at it by 200 times using the usual optical microscope. A raw material alloy is embedded to resi etc., is ground in detection of an organization, and it does not take detection especially according to etching fluid etc using as it is what finished the longitudinal section in the shape of a mirror plane by finishing buffing.

[0032] The visual field to observe chooses ten visual fields of cross-section organizations by the side of roll side clos attendants at random, and takes a longitudinal-section organization photograph by 200 times. In these cross-section organization photographs, a straight line is drawn in location of 20mm (photograph top absolute size) from a roll sid side, and the number of the primary arms which cross the straight line is counted. It ** by the number which counted the sample absolute size equivalent to the die length of the straight line, and considers as primary dendrite arm spacin

[0033] In order to obtain the raw material alloy for R-T-B system magnets which has an above-mentioned alloy organization, it is desirable for the thickness of a cast piece to be 0.1-10mm. In less than 0.1mm, the cooling effect becomes excessive, and the generation ratio of a chill crystal exceeds 5%, the cooling effect is not fully demonstrated in 10mm or more, but there is a problem which causes big-and-rough-izing of solidification structure and generation alpha-Fe. From the viewpoint, the thickness of a still more desirable cast piece is 0.2-5mm.

[0034] The raw material alloy for R-T-B system magnets manufactured by the above-mentioned approach is manufactured by the permanent magnet with a good magnet property by performing the powder metallurgy process described below, i.e., grinding, shaping among a magnetic field, sintering, and heat treatment.

[0035] It is desirable to give preliminary grinding (hydrogen grinding) by the hydrogenation-dehydrogenation to grinding. A hydrogen treating introduces hydrogen gas, after setting the raw material alloy for R-T-B system magnet to a vacua within a chamber etc., after holding it at least 5 minutes or more, it leads it to a vacuum once again, inert gas such as Ar gas, permutes it if needed, and it is processed by cooling to a room temperature. Preliminary grinding is given by performing dehydrogenation treatment after a hydrogen treating. Dehydrogenation treatment is processed b cooling to a room temperature, after holding 30 minutes or more in a vacuum at 100 degrees C - 600 degrees C.

[0036] Grinding by the jet mill is given after above-mentioned preliminary grinding. Dry type or wet attritor or a ball mill may be used for grinding. The average powder grain size after grinding has desirable 2-8 micrometers. In order that a less than 2-micrometer impalpable powder particle may tend to oxidize during grinding and average grain size may reduce a magnet property, it cannot be used, but there is a problem of causing the fall of the yield as a result. Th is a problem that, as for a particle, average grain size causes the fall of coercive force in the coarse powder end of 8-micrometer ** in order to make the grain structure of a sintered magnet big and rough. From this viewpoint, a more desirable average grain size is 2-4 micrometers.

[0037] By performing a series of above-mentioned grinding processings to the raw material alloy for R-T-B system magnets of this invention, the powder which has a good particle-size-distribution property with little impalpable powder compared with the conventional material is obtained. In shaping among a magnetic field, it is filled up with t powder of the raw material alloy for R-T-B system magnets obtained by the above-mentioned approach by the mold made from austenite steel, the mold made of rubber, for example, the product, of a non-magnetic material, or martensitic steel, and after carrying out orientation of the powder particle by impressing a pulsed magnetic field, it fabricates with a press. Moreover, a static magnetic field or a pulsed magnetic field, and a static magnetic field may combined instead of a pulsed magnetic field.

[0038] Sintering is processed at 1030 degrees C - 1150 degrees C in a vacuum or Ar inert gas ambient atmosphere fo to 4 hours. The permanent magnet of this invention is manufactured by performing aging heat treatment for 30 - 90 minutes at 450 degrees C - 650 degrees C if needed after that. Moreover, the raw material alloy for magnets manufactured by this invention is possible also for application in a HDDR process, and usable also to a bond magnet [0039]

[Example]

The alloy of the presentation shown in example 1 table 1 was once decompressed to 0.01Torr(s), and it dissolved by high-frequency induction heating in the ambient atmosphere which poured in Ar gas up to gage pressure 0.2 atmospheric pressure. The rapid solidification cast piece was produced with the congruence roll quenching equipmen shown in drawing 3 using this molten metal. The surface of hot water 7 goes up gradually as drawing 3 is what show rapid solidification equipment typically, and teeming is carried out from the tundish 5 upper part, and a molten meta once accumulated in tundish 5 and carries out teeming, and it is **. It overflows from the tundish weir 6 and results roll 8. The roll 8 has rotated in the direction of the arrow head in drawing beforehand, rapid solidification is carried o

with a roll 8, and the rapid solidification cast piece 9 is produced.

[0040] The diameter of a roll shall be 600mm and the base material shall show the quality of the material of the surface layer in Table 2 and 5 using a copper beryllium alloy. Moreover, the gap during a roll was adjusted so that it might be set to 1-2mm. In addition, although this example was explained by the case where a congruence roll is used, even when a single roll was used, it was checked that the same effectiveness had been acquired.

[0041] The obtained cast piece was held in 3kg/cm² H₂ gas ambient atmosphere for 2 hours, and carried out the hydrogen treating to it, and it held at 500 degrees C among the vacuum after that for 5 hours, dehydrogenation treatment was performed, and it considered as preliminary grinding by cooling to a room temperature. About magnet field shaping, the mold made of rubber was filled up with the obtained powder, and after carrying out orientation of the powder by impressing the pulsed magnetic field of 30kOe momentarily, the hydrostatic-pressure press was given. After holding this Plastic solid in 3 hours and sintering it at 1090 degrees C, aging heat treatment of 1 hour was performed at 600 degrees C, and the permanent magnet was obtained.

[0042] As the chill crystal yield of the cast piece obtained by the approach of this invention was shown in Table 3 and 6, it was 5% or less, and primary arm spacing of a columnar crystal was set to 3.2-7 micrometers, the detailed powder yield after grinding was low, and the magnetic maximum energy product was greatly good compared with the example of a comparison.

[0043] The same trial as an example was performed using the thing with the copper beryllium alloy which is a base material, without reforming the peripheral face of an example of comparison 1 quenching roll. It is shown in Table 4 making the result into the example of a comparison. Although spacing of a primary DIN light arm was the same as that of an example, the yield of a chill crystal was over 5%, the fines yield was also high and the magnet property was also that in which a maximum energy product is small inferior as compared with an example.

[0044] The same trial as an example was performed using the quenching roll which reformed the peripheral face by plating with an example of comparison 2 thickness of 50 micrometers. The result is shown in Table 4. In Cr plating, since effectiveness of gradual-cooling-izing cannot fully be acquired, there is a problem on which the yield of a chill crystal exceeds 5%, impalpable powder is generated, and the yield is reduced, and also it is clear that a magnet property is also inferior as compared with the example of this invention.

[0045]

[Table 1]

| (at%) | | | | | | |
|-------|------|----|-----|-----|----|---|
| 合金名 | Nd | Pr | Dy | Fe | Co | B |
| 合金1 | 14.5 | 0 | 0 | bal | 0 | 6 |
| 合金2 | 9.0 | 3 | 2.5 | bal | 0 | 6 |
| 合金3 | 14.5 | 0 | 0 | bal | 3 | 6 |

[0046]

[Table 2]

| 区分 | ロール名 | 表面改質の種類 | 厚み(mm) |
|-------|-------|--------------------------------------------|---------------------|
| 本発明1 | ロール1 | Niメッキ | 1 |
| 本発明2 | ロール2 | Niメッキ | 2.5 |
| 本発明3 | ロール3 | Niメッキ | 5 |
| 本発明4 | ロール4 | Mo溶射 | 2.5 |
| 本発明5 | ロール5 | Niメッキ アルミナ溶射 | 0.5(下地) 0.5(最表面) |
| 本発明6 | ロール6 | Niメッキ TiN溶射 | 0.5(下地) 1.0(最表面) |
| 本発明7 | ロール7 | WC-17Co溶射 | 3 |
| 本発明8 | ロール8 | W-Cu溶射 | 3 |
| 本発明9 | ロール9 | Niメッキ SiC溶射 | 0.5(下地) 2(最表面) |
| 本発明10 | ロール10 | Niメッキ AlN溶射 | 0.5(下地) 2(最表面) |
| 本発明11 | ロール11 | Fe-Ni-Cu溶射 | 4 |
| 本発明12 | ロール12 | Niメッキ Si ₃ N ₄ 溶射 | 0.5(下地) 1(最表面) |
| 本発明13 | ロール13 | Niメッキ ジルコニア溶射 | 0.5(下地) 1(最表面) |
| 本発明14 | ロール14 | SiC-Ni複合溶射 溶射後HIPにより緻密化処理 | 3 |
| 比較例1 | ロール15 | 表面改質なし(銅ベリリウム合金のまま) | |
| 比較例2 | ロール16 | Crメッキ | 0.05 |

[0047]
[Table 3]

| ロール | 合金 | チル晶平均 生成率(%) | 柱状晶平均 一次アーム 間隔(μm) | 微粉末 生成率 (%) | 磁石特性 | | |
|-------|-----|-----------------|--------------------------|-------------------|----------|-----------------|------------|
| | | | | | Br kG | (BH)max MGOe | iHc kOe |
| ロール1 | 合金1 | 2.0 | 3.2 | 0.5 | 14.1 | 48.7 | 12.8 |
| ロール2 | 合金1 | 0.8 | 5.0 | 0.2 | 14.2 | 49.4 | 12.5 |
| ロール3 | 合金1 | 0.3 | 6.1 | 0.1 | 14.3 | 50.1 | 12.3 |
| ロール4 | 合金1 | 0.5 | 4.8 | 0.2 | 14.2 | 49.3 | 12.5 |
| ロール5 | 合金1 | 0.2 | 7.0 | 0.1 | 14.2 | 49.2 | 12.4 |
| ロール6 | 合金1 | 0.2 | 6.2 | 0.1 | 14.3 | 49.9 | 12.2 |
| ロール7 | 合金1 | 1.3 | 4.2 | 0.4 | 14.1 | 48.8 | 13.0 |
| ロール8 | 合金1 | 1.5 | 5.1 | 0.4 | 14.1 | 48.6 | 12.6 |
| ロール9 | 合金1 | 0.8 | 6.1 | 0.2 | 14.2 | 49.1 | 12.2 |
| ロール10 | 合金1 | 0.7 | 5.9 | 0.2 | 14.2 | 49.3 | 12.6 |
| ロール11 | 合金1 | 1.2 | 3.8 | 0.3 | 14.1 | 48.7 | 13.0 |
| ロール12 | 合金1 | 0.4 | 6.2 | 0.1 | 14.3 | 50.2 | 12.2 |
| ロール13 | 合金1 | 0.5 | 6.0 | 0.2 | 14.3 | 50.0 | 12.4 |
| ロール14 | 合金1 | 1.0 | 6.3 | 0.3 | 14.1 | 48.5 | 12.8 |
| ロール2 | 合金2 | 0.6 | 4.1 | 0.2 | 12.7 | 39.4 | 23.2 |
| ロール2 | 合金3 | 0.8 | 5.5 | 0.2 | 14.2 | 49.2 | 12.6 |

[0048]

[Table 4]

| ロール | 合金 | チル晶平均 生成率(%) | 柱状晶平均 一次アーム 間隔(μm) | 微粉末 生成率 (%) | 磁石特性 | | |
|-------|-----|-----------------|--------------------------|-------------------|----------|-----------------|------------|
| | | | | | Br kG | (BH)max MGOe | iHc kOe |
| ロール15 | 合金1 | 9.2 | 6.1 | 1.9 | 13.6 | 45.3 | 11.7 |
| ロール15 | 合金2 | 14.3 | 3.8 | 2.8 | 12.2 | 36.4 | 21.9 |
| ロール15 | 合金3 | 10.1 | 4.9 | 1.7 | 13.5 | 44.8 | 11.4 |
| ロール16 | 合金1 | 7.6 | 5.5 | 1.7 | 13.5 | 45.0 | 11.5 |

[0049]

[Table 5]

| ロール名 | 表面改質の種類 | 厚み (mm) |
|-------|------------------------------------------------------------------------------------------------|---------------------|
| ロール17 | Ni-50Cr溶射(wt%) | 2.5 |
| ロール18 | Co-23Cr-12Al-0.5Y溶射(wt%) | 2.5 |
| ロール19 | Co-32Ni-21Cr-8Al-0.5Y溶射(wt%) | 2.5 |
| ロール20 | Ni-22Cr-10Al-1Y溶射(wt%) | 2.5 |
| ロール21 | Co-28Cr-4W-3Fe-1C溶射(wt%) | 2.5 |
| ロール22 | Co-28Mo-17Cr-3Si溶射(wt%) | 2.5 |
| ロール23 | WC-12Co溶射(wt%) | 1.0 |
| ロール24 | WC-17Co溶射(wt%) | 1.0 |
| ロール25 | WC-27Co溶射(wt%) | 1.0 |
| ロール26 | WC-27NiCr溶射(wt%) | 1.0 |
| ロール27 | Niメッキ Al ₂ O ₃ -3TiO ₂ 溶射(wt%) | 0.5(下地) 0.5(最表面) |
| ロール28 | Niメッキ Al ₂ O ₃ -25ZrO ₂ -2TiO ₂ 溶射(wt%) | 0.5(下地) 0.5(最表面) |
| ロール29 | Niメッキ Al ₂ O ₃ -22Si溶射(wt%) | 0.5(下地) 0.5(最表面) |
| ロール30 | Niメッキ ZrO ₂ -8Y ₂ O ₃ 溶射(wt%) | 0.5(下地) 0.5(最表面) |
| ロール31 | Niメッキ ZrO ₂ -25MgO溶射(wt%) | 0.5(下地) 0.5(最表面) |
| ロール32 | WC-14CoCr溶射(wt%) | 0.2 |
| ロール33 | Cr ₃ C ₂ -25NiCr溶射(wt%) | 0.2 |
| ロール34 | Niメッキ NiCr-40ZrO ₂ -40Y ₂ O ₃ | 0.5(下地) 0.2(最表面) |
| ロール35 | Niメッキ Co-32Ni-21Cr-8Al-0.5Y-40ZrO ₂ - 40Y ₂ O ₃ 溶射(wt%) | 0.5(下地) 0.2(最表面) |
| ロール36 | Niメッキ ZrO ₂ -33SiO ₂ 溶射(wt%) | 0.5(下地) 0.2(最表面) |
| ロール37 | Niメッキ Cr ₃ C ₂ 溶射(wt%) | 0.5(下地) 0.2(最表面) |
| ロール38 | Niメッキ TiC溶射(wt%) | 0.5(下地) 0.2(最表面) |
| ロール39 | Niメッキ ZrC溶射(wt%) | 0.5(下地) 0.2(最表面) |
| ロール40 | Niメッキ ZrB ₂ 溶射(wt%) | 0.5(下地) 0.2(最表面) |

[0050]

[Table 6]

| | ロール名 | 合金 | チル晶 平均 生成 率(%) | 柱状晶 の平均 1次アーム 間隔(μm) | 微粉末 生成 率(%) | 磁石特性 | | |
|---|-------|-----|-------------------------|-------------------------------|-------------------|------------|-------------------|--------------|
| | | | | | | Br (kG) | (BH)max (MGOe) | iHc (kOe) |
| 本 | ロール17 | 合金1 | 0.8 | 5.1 | 0.2 | 14.1 | 49.5 | 12.6 |
| | ロール18 | 合金1 | 0.7 | 5.2 | 0.2 | 14.1 | 49.4 | 12.5 |
| | ロール19 | 合金1 | 0.9 | 5.0 | 0.2 | 14.0 | 49.5 | 12.6 |
| | ロール20 | 合金1 | 0.7 | 5.1 | 0.2 | 14.2 | 49.5 | 12.4 |
| | ロール21 | 合金1 | 0.8 | 5.0 | 0.2 | 14.0 | 49.3 | 12.5 |
| | ロール22 | 合金1 | 0.7 | 5.2 | 0.1 | 14.1 | 49.4 | 12.5 |
| | ロール23 | 合金1 | 1.2 | 4.7 | 0.3 | 14.1 | 49.5 | 12.6 |
| | ロール24 | 合金1 | 1.0 | 4.5 | 0.2 | 14.2 | 49.8 | 12.7 |
| | ロール25 | 合金1 | 0.9 | 4.4 | 0.2 | 14.2 | 49.9 | 12.8 |
| | ロール26 | 合金1 | 0.9 | 4.5 | 0.2 | 14.1 | 49.7 | 12.7 |
| 発 | ロール27 | 合金1 | 0.5 | 5.3 | 0.1 | 14.0 | 49.8 | 12.6 |
| | ロール28 | 合金1 | 0.4 | 5.3 | 0.1 | 14.0 | 49.7 | 12.5 |
| | ロール29 | 合金1 | 0.5 | 5.2 | 0.2 | 14.1 | 49.8 | 12.6 |
| | ロール30 | 合金1 | 0.4 | 5.3 | 0.1 | 14.2 | 49.8 | 12.6 |
| | ロール31 | 合金1 | 0.6 | 5.1 | 0.2 | 14.0 | 49.9 | 12.7 |
| | ロール32 | 合金1 | 1.0 | 4.4 | 0.2 | 14.1 | 49.7 | 12.7 |
| | ロール33 | 合金1 | 1.1 | 4.2 | 0.2 | 14.1 | 49.6 | 12.6 |
| | ロール34 | 合金1 | 0.9 | 4.7 | 0.2 | 14.0 | 49.6 | 12.4 |
| | ロール35 | 合金1 | 0.9 | 4.6 | 0.2 | 14.2 | 49.7 | 12.4 |
| | ロール36 | 合金1 | 0.8 | 4.7 | 0.1 | 14.1 | 49.5 | 12.3 |
| 明 | ロール37 | 合金1 | 0.9 | 4.9 | 0.2 | 14.1 | 49.2 | 12.2 |
| | ロール38 | 合金1 | 0.9 | 4.8 | 0.2 | 14.0 | 49.3 | 12.3 |
| | ロール39 | 合金1 | 0.8 | 4.5 | 0.2 | 14.2 | 49.7 | 12.6 |
| | ロール40 | 合金1 | 0.7 | 4.9 | 0.1 | 14.1 | 49.2 | 12.3 |

[0051]

[Effect of the Invention] This invention made it possible to be able to control generation of a detailed chill crystal organization, consequently to prevent generation of the impalpable powder in a grinding process, and to obtain the powder for shaping of good particle size distribution by preparing the surface layer of the according to ingredient with thermal conductivity smaller than base material to roll surface variously on the occasion of manufacture of raw material alloy for R-T-B system magnets of presentation specification thickness manufactured by the rapid-solidification method which used the roll for cooling, and attaining gradual-cooling-ization. Furthermore, it made it possible to of a R-T-B system magnet with a good magnet property by performing shaping, sintering, and aging heat treatment using the powder for shaping.

[Translation done.]